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TASK I

VINYLIDENE CHLORIDE

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16. ABSTRACT

Recent reports of the possible carcinogenic properties of vinylidene chloride, because of structural similarity to vinyl chloride, prompted this investigation. This report views the chemical and physical properties of vinylidene chloride (VDC) and its important derivitives and polymers. A detailed discussion of the manufacturing process, including sites, new technologies and environmental management is presented. The consumption of VDC in the manufacture of methyl chloroform and alternative manufacturing processes for methyl chloroform which do not involve VDC are discussed. The most important end use of VDC, polymerization, is described in detail. A cost performance analysis of copolymers containing VDC, VDC laminated films, multilayer "PVDC sandwich" type films and other films not containing VDC such as polyethylene and polyproplene is reported. Finally a summary of the chemical losses due to air emissions, liquid effluents and solid wastes is discussed.

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TASK I

VINYLIDENE CHLORIDE

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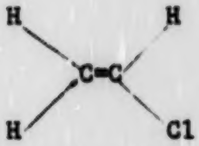
SECTION I. STATUS AND OUTLOOK SUMMATION

1.0 OBJECTIVE AND SCOPE OF THE REPORT

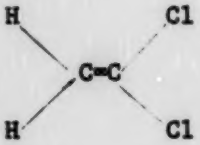
Vinylidene chloride (VDC) has been in extensive commercial use since the early 1940's, when copolymerization and plasticization techniques were developed at Dow Chemical Company. The chief resultant copolymers of VDC, known as saran or polyvinylidene chloride, have been produced continuously since that time.

Saran exhibits certain physical properties which render it ideally suited for use as a packaging film or barrier coating on other materials used in the food packaging industry. These properties include high barrier resistance to water vapor and other gases such as oxygen and carbon dioxide, grease and oil resistance, and flavor retention. In addition, saran is free of taste and odor, has good heat seal properties, is flexible and abrasion resistant and has good printing qualities. Although a number of other polymers can act as a substitute for saran in its applications as a packaging film or barrier coating, none possess the same barrier resistance to both oxygen and water vapor for a given film thickness.

The discovery in the early 1970's that vinyl chloride was a carcinogen at relatively low concentrations (20 ppm)* for chronic exposures, prompted a reexamination of other chemicals which had previously been regarded as safe, or having only acute toxicity effects at high concentrations. Vinylidene chloride came under examination because of its structural similarity to vinyl chloride:



Vinyl Chloride



Vinylidene Chloride

However, as will be evident from Section II, its physical and chemical properties are significantly different.

More recently, concern has arisen over the possibility of the migration of residual traces of monomers from their polymers. In this connection, both vinylidene chloride and acrylonitrile were specifically singled out.

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*National Institute for Occupational Safety and Health, 1975. Registery of Toxic Substances, p. 534.

It is because of the history of vinyl-type monomers and their associated health problems that this research study was undertaken. The objective of the report is to present a detailed analysis regarding the production, consumption and losses to the environment of vinylidene chloride. Most but not all aspects of the study are addressed directly. Its scope includes a detailed discussion of the current manufacturing sites and processes for VDC, its associated shipping and handling practices, production markets, and environmental management during production. An equally detailed presentation of the consumption processes and sites, environmental management of the monomer in the various consumption processes, and the consumption markets for polyvinylidene chloride are also given. However, the materials history for the past ten years could not be presented directly, since production figures for neither VDC nor its copolymers are reported separately to the U.S. International Trade Commission; the individual producers and consumers regard these figures as highly proprietary and would not divulge them to AAI. Thus, estimates in this area are based on documented assumptions and calculations, and are identified as such. The toxicology of VDC and PVDC and related impacts on human health are not within the scope of this report.

The information presented in the report was collected from many sources. Most important were the on-site and telephone interviews conducted with the producers of VDC, the producer of 1,1,1-trichloroethane (1,1,1-TCE) from VDC, the polymerizers of VDC, and representatives of the companies converting or otherwise handling VDC-containing polymers. In addition, data were obtained from the published literature, from trade associations, and representatives of state and federal agencies. The degree to which certain data were regarded as confidential, and the level of cooperation obtained, varied widely among the industries concerned and the individual companies contacted. This is reflected in the degree of accuracy in the data reported by the various companies contacted in the course of the study.

1.1 MANUFACTURE AND DISTRIBUTION OF VINYLIDENE CHLORIDE

Vinylidene chloride is one of a number of chemicals which are produced directly or indirectly from the chlorination of ethylene or ethane. It is currently manufactured domestically by two companies, PPG Industries and Dow Chemical Company, at an annual rate of approximately 270 million pounds.

1.1.1 Manufacturing Processes and Sites

PPG currently produces about 170 to 180 million pounds of VDC annually at its plant in Lake Charles, La. Dow Chemical Co., produces about 100 million pounds per year at two plant locations, Freeport, Texas and Plaquemine, La. It is reported that the Freeport plant produces about two-thirds of Dow's annual production.

Vinylidene chloride is made either as a coproduct of ethylene dichloride, produced from the chlorination of ethane or ethylene, or by the dehydrochlorination of 1,1,2-trichloroethane according to the following reaction:

$$CH_2Cl\text{-}CHCl_2 + NaOH \longrightarrow CH_2 = CCl_2 + NaCl + H_2O$$

Dow uses both processes. The choice is economic and varies with market demand and prices of the coproducts.

PPG currently produces VDC from the dehydrochlorination of 1,1,2-trichloroethane.

1.1.2 Sales and Distribution

Both PPG and Dow consume captively about 85% of the total VDC manufactured each year. The balance, or about 40 to 50 million pounds, enters the merchant market. PPG uses about 130 million pounds of VDC to produce 1,1,1-trichloroethane; Dow uses about 80 to 90 million pounds to produce various polymers of VDC.

Approximately 11 companies buy VDC monomer from either PPG or Dow to produce a wide variety of polymeric products containing VDC.

Because of hazards inherent in the storage and handling of VDC, storage is limited to the amount needed to meet the operating demand of the consumer companies. This, combined with a reasonably stable supply situation, makes stockpiling VDC monomer infeasible.

1.1.3 Shipping and Handling

VDC is usually shipped in bulk railroad tank cars or tank trucks. A small quantity is shipped in drums. To prevent the formation of peroxides and spontaneous polymerization, VDC is shipped inhibited (usually with monomethyl ether of hydroquinone) and under a nitrogen blanket. Even under these conditions, it is recommended that storage not exceed four months.

Tank cars or tank trucks used to transport VDC are dedicated to that service. Suitable precautions in loading and unloading transport equipment should be used to prevent contact with air or water. Copper, aluminum and their alloys should not be used in contact with VDC monomer.

Stainless steel or nickel are the recommended materials of construction for storage containers. Non-lubricated valves and fittings are specified.

1.1.4 Environmental Fate

VDC emitted to the air during manufacture or its subsequent polymerization is reported to react, under specific conditions, to form peroxide and epoxide compounds which tend to decompose spontaneously to form HCl, $CCCl_2$, various oxygenated organic chlorides, ethylene dichloride and chlorinated olefins. The bulk (75%) of VDC loss emissions are process derived; the balance result from storage, transfer and filling operations.

Based on data supplied by the producing companies, total VDC losses during manufacture are in the range of 0.0012 to 0.0031 lbs. per pound produced.

Table 1-1 summarizes estimated production, consumption and environmental manufacturing losses for 1975-76.

1.1.5 Market Factors

Based on the present evaluation of the market, it is estimated that approximately 130 million pounds of VDC are consumed captively in the production of 1,1,1-TCE, 135 million pounds are polymerized, and 5 million pounds are used as a chemical intermediate.

The demand for VDC polymers has grown at an average rate of 5 percent per year since 1970. Since the major application of PVDC is in the production of flexible film for food packaging, demand for the polymer is closely tied to the market requirements and economic constraints of this industry. Although this market is growing rapidly, chiefly in the area of snack and convenience foods, the changing pattern of packaging materials is such that the future growth of VDC for polymerization is expected to continue at about the same level as the general economic growth.

The demand for VDC as a raw material for 1,1,1-TCE appears to have increased since PPG built its plant in 1967. PPG is the only company presently manufacturing 1,1,1-TCE from VDC. It is reported that when PPG's new plant for 1,1,1-TCE is put into operation in 1978, it will use a new process that does not have VDC as the feed stock. PPG will no longer have a captive use for its VDC. However, according to industry reports, PPG will maintain facilities capable of producing an anticipated 75 million pounds of VDC per year for merchant sales to polymerizers.

1.2 CONSUMPTION OF VDC FOR 1,1,1-TRICHLOROETHANE (METHYL CHLOROFORM)

1.2.1 Consumption Processes and Sites

1,1,1-TCE is manufactured at PPG's chlorinated hydrocarbon complex plant in Lake Charles, La., by hydrochlorination of VDC, according to the following reaction:

TABLE 1-1. INPUT/OUTPUT SUMMARY FOR VINYLIDENE CHLORIDE MANUFACTURE 1976

Company	Site	Estimated Capacity	VDC Sales Distribution 10^6 lbs/yr		VDC End Use Patterns 10^6 lbs/yr			Estimated Manufacturing Losses lbs/year
		10^6 lbs/yr	Captive	Merchant	1,1,1-TCE	Polymers	Chemical Intermediate	
PPG	Lake Charles, La.	170 - 180	140 - 150	20 - 25	140 - 150	20 - 25		200,000 - 300,000
DOW	Plaquemine, La.	95 - 100	75 - 85	15 - 20	---------	95 - 100	5	238,000
	Freeport, Tx.							100,600
TOTAL		265 - 280	215 - 230	35 - 45	140 - 150	115 - 125	5	538,600 - 638,600

$$CH_2 = CCl_2 + HCl \longrightarrow CH_3CCl_3$$

This is the only site at which 1,1,1-TCE is produced from VDC. 1,1,1-TCE is also manufactured by Dow Chemical Company and Vulcan Chemicals using other routes for its manufacture which include chlorination of vinyl chloride, or direct chlorination of ethane. The specific process used by the various manufacturers is dependent on the company's proprietary technology, the desired product mix, and the economics of the overall operation.

1.2.2 Environmental Fate

Losses of VDC from the PPG plant during the production of 1,1,1-TCE are reported to be non-existent, because the process is continuous and all equipment is interconnected. Unreacted VDC and HCl are separated from the hydrochlorination product stream by distillation and recycled to the hydrochlorinator for further reaction. The product is reported to contain a maximum of 100 ppm VDC. Based on an estimated production of 1,1,1-TCE from VDC of 175 million pounds in 1976, the possible amount of VDC monomer in the 1,1,1-TCE sold in the U.S. could equal 17,500 pounds per year. The commercial distribution of 1,1,1-TCE is so wide-spread that local concentrations of VDC monomer would not exceed an order of magnitude of 0.006 pounds per square mile.*

1.2.3 Distribution and Market Factors

1,1,1-TCE has many commercial uses and its distribution ranges from large industrial users to small commercial establishments. From 1963 to 1973 the overall demand for 1,1,1-TCE grew at an average rate of about 10 percent, dropping to an average of 2.5 percent per year over the period 1973 to 1976. This slowdown in demand was attributed to the setbacks to the U.S. economy with resultant decreased demand for such items as appliances, automobiles, housing and other metal fabrication products that require a degreasing operation. Although the demand for VDC as a raw material for 1,1,1-TCE has increased since 1967, paralleling PPG's sales, it is expected to drop to nil when PPG's new process for 1,1,1-TCE becomes operational in 1978.

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*Calculated using area of continental U.S. equal to 2.98×10^6 sq. mi.

1.3 CONSUMPTION OF VDC IN POLYMERIZATION PROCESSES

Vinylidene chloride monomer is copolymerized with other monomers to form a variety of products with specific properties. Polymers containing more than 50% VDC, usually in the range of 70 to 95%, exhibit superior barrier properties to oxygen, water vapor and other gaseous materials, and are chemically inert. The comonomers most used in this application are vinyl chloride, acrylic acid, and acrylonitrile. This type of VDC copolymer may be used as a latex to coat various film substrates such as paper products, polyester, polypropylene or polyethylene to improve the barrier properties of the substrates. It may also be converted into a film (saran) and used as such or laminated to other plastic films. Again these films are used where superior barrier properties are desired.

VDC is used in polymers containing less than 50% VDC, usually in the range of 10 to 40% in order to improve the flame retardant properties of the base polymer. Typical of this application are copolymers with butadiene-styrene, used as carpet backing, and the modacrylic fibers.

There are some minor applications of VDC polymers for pipe or pipe liner due to their chemical resistance.

1.3.1 Polymerization Processes and Sites

Vinylidene chloride polymers, like polymers of vinyl chloride, are produced using either emulsion or suspension polymerization techniques. Resin powder is prepared by filtering or centrifuging the polymer obtained by emulsion or suspension techniques, and drying the resultant wet solids. The two polymerization techniques use essentially similar equipment. The processes differ in such details as the type and quantity of surface active agents used, the operating conditions, and stripping techniques.

The reactants (VDC, comonomer, catalyst, emulsifier or suspending agent, and water) are fed into an evacuated reactor. The batch is heated and agitated for between 8 and 24 hours until the desired degree of polymerization is obtained (90 to 98%). The polymerized batch is stripped of unreacted monomer (in situ or transferred to a stripper vessel) using steam and vacuum. The stripped VDC monomer may be recovered and recycled, vented to a disposal system or vented to the atmosphere.

Solvent polymerization has been used in the copolymerization of VDC with other monomers such as acrylonitrile to produce a textile fiber by the use of wet spinning processes. A more generally used process is to manufacture the dry polymer in conventional equipment, dissolve the resin in a suitable solvent and then use a wet spinning process.

There are approximately 13 sites where VDC is polymerized. The sites and polymer produced are shown in Table 1-2. The polymerization processes, products and end products are shown in Table 1-3.

1.3.2 PVDC Converting Processes, Sites and End Products

PVDC is sold to convertors as either an emulsion latex or a solid resin. At present only one converter, DuPont, polymerizes VDC for captive use.

Emulsion latexes are sold to companies who convert paper products and plastic film into packaging materials. These companies use the latexes to coat the substrate film with a thin (1 to 3 mil thick) layer of PVDC to provide improved barrier properties to oxygen and water vapor.

TABLE 1-2. POLYMERIZATION SITES AND TYPE OF POLYMER PRODUCED

Company	Location	Polymer Type	Estimated VDC Consumption Capacity (millions of pounds)
Dow Chemical Co.	Midland, Mi.	Latex Suspension Latex Emulsion Soild Resin	>10
	Dalton, Ga.	Latex Emulsion	5
W.R. Grace Chemical Company	Owensburg, Ky.	Specialy Latex Latex Emulsion	>10
Morton Chemical Co.	Ringwood, Ill.	Latex Emulsion	>10
A.E. Staley Mfg. Co.	Lemont, Ill.	Latex Emulsion	5
Rohm and Haas Co.	Knoxville, Te.	Latex Emulsion	<1
GAF Corporation	Chattanooga, Te.	Latex Emulsion Specialty Latex	<1
Reichhold Chemical	Cheswold, De.	Latex Emulsion Specialty Latex	<1
National Starch and Chemical	Meridosia, Ill.	Latex Emulsion Specialty Latex	<1
Tennessee Eastman	Kingsport, Te.	Modacrylic Fiber	10
Monsanto Chemical Co.	Decatur, Al.	Modacrylic Fiber	5 to 10
American Cyanimide	Pensacola, Fl.	Modacrylic Fiber	<5
E.I. DuPont	Circleville, Oh.	Solid Resin	5

TABLE 1-3. POLYMERIZATION PROCESSES, PRODUCTS AND END PRODUCTS

PROCESS	PRODUCT	END PRODUCT
Emulsion Polymerization	Latex Emulsion	Barrier coating on plastic films and paper products Fire retardant carpet backing
	Resin	Barrier coating Molded plastics Extruded films and pipe
Suspension Polymerization	Resin	Solution coating for barrier properties Molded plastics Extruded film and pipe
Solution Polymerization	Fiber (modacrylics)	Flame retardant textiles

Because coating of packaging film substrate is a normal part of a converting line, there are a substantial number of sites where PVDC latexes are used or can be used, depending upon the demand. The major converters and plant sites are given in Table 4.4 (see Section 4.2).

PVDC resin has three uses; (1) for solvent coating of plastic film and cellophane (2) for film extrusion, and (3) for molding.

Solvent coating of cellophane with PVDC is limited to three companies, Olin, DuPont and FMC, at three sites.

This process comprises dissolving solid resin in a suitable solvent, coating the cellophane, removing solvent in a drying oven, conditioning the coated, dried film and winding the coated film for shipment to packaging converters. The solvent removed in the drying step is recovered and recycled.

Except for Dow Chemical Co., none of the film producers make a PVDC resin. Conventional plastic film making techniques are used in PVDC film manufacture. PVDC film may be produced by using either a flat extrusion process or blown film techniques. The latter process can produce a "biaxially" oriented "shrink film". There are four manufacturers of PVDC film for merchant sale and several captive film producers.

Specialty butadiene-styrene latexes containing less than 50% VDC find their greatest outlet as a flame retardant carpet backing sold to carpet and rug manufacturers. There are a large number of companies capable of applying this type of latex as a backing.

There are no "by-products" as such for these converting processes. The PVDC waste products of packaging converting operations, consist of scrap film. Losses of this nature can range from 25 to 50 percent based on film weight.

1.3.3 Environmental Fate of VDC in Polymerization Process

Losses of VDC monomer during polymerization can result from the following:

(1) Vent losses during transfer of monomer feed to and from storage tanks and reactors.

(2) Losses to the atmosphere from stripping operations, where unreacted monomer is reduced to lowest possible levels in the polymer emulsion product.

Minor losses of VDC monomer can occur as a contaminant in polymer sewered during periodic washing of reactor and stripping vessel, as well as from the disposal of unuseable (bad) batches.

Substantially 98% of VDC emissions from polymer plants result from the stripping of unreacted monomer from the finished polymer latex. Control methods include:

(1) Modification of the polymerization process to minimize the amount of unpolymerized VDC remaining in the batch.

(2) Installation of systems to recover VDC monomer from the stripper vent gases.

(3) Installation of incineration systems to destroy the VDC in the vent gases.

Almost all manufacturers of polyvinylidene chloride are striving to decrease the amount of unreacted VDC monomer left after the polymerization reaction. The criteria for installing either VDCM recovery systems or incineration equipment are economic, and related to the size of the VDC polymer plant. At present, only the largest polymer producers have found it economically feasible to install either of the latter two methods to control VDC emissions.

On the basis of reported polymerization losses from the smaller polymer producers of 0.6% to 1.2%, emissions would range from 16 lbs. per day per million pounds VDC polymerized annually to 32 lbs. per day. Hence a plant polymerizing 10 million pounds per year of VDC would probably vent about 200 pounds of VDC per day.

For those plants producing specialty latexes, such as the VDC formulated flame retardant carpet backing, where conversion rate is the lowest (90%) and VDC concentration in the feed is lowest (under 40%) we find that the pounds of VDC emitted per 100 lbs. VDC polymerized are on the order of 1.26 for the largest and 2.8 for the smallest companies. At present, the amount of VDC used in these polymers is low (estimated at 7 to 9 million pounds per year) and based on an average loss of 1.5%, the probable total loss from this source is calculated to be between 105,000 and 135,000 pounds per year.

It has been estimated that a total of about 520,000 pounds of VDC monomer were lost to the atmosphere in 1975 from polymerization operations conducted at 13 sites. One of the major polymerizers reported that the plant that produces more than 60% of their VDC polymers has reduced emission losses from about 4000 lbs. per day in 1972 to probably less than 200 lbs. per day in 1977.

Other VDC monomer losses occur in the liquid wastes disposed by polymer manufacturers to sewerage disposal facilities. This loss is estimated to be between 3000 and 4000 pounds per year.

1.3.4 Disposal and Ultimate Fate of the Polymer

Over 95 percent of VDC polymers are used for packaging, in the manufacture of textile fibers or as a component of flame retardant carpet backing. These are all consumable items that are thrown away at the end of their useful life. The ultimate disposal is either the incinerator or solid waste land fills. Only a small percentage of the PVDC enters the capital goods industry (chiefly as pipe or a lining in pipe) where the useful life is relatively long.

Over the past 10 years it is estimated that between 700 million and 1 billion pounds of PVDC have been ultimately disposed in the manner noted above. Based on an estimated VDC monomer content of the converted polymer ranging from a possible maximum of 60 ppm in 1966 to under 5 ppm in 1976, it can be postulated that between 25,000 and 50,000 lbs. of VDC monomer could have entered the environment from the finished products during the past 10 years.

1.3.5 Environmental Fate of VDC During Converting Processes

Significantly lower levels of VDC monomer in PVDC latexes and solid resins have been achieved by the polymerizers since 1971. One company stated they have reduced the content of VDCM in polymer emulsions from over 600 ppm in 1971 to about 25 ppm in 1976. The average VDCM content of the polymers currently produced in the U.S. is on the order of 50 ppm for the latexes and 20 ppm for the resins. Based on this range of monomer content, and an average yearly VDC polymer production (exclusive of specialty polymers and fibers) equal to 85 million pounds, it can be calculated that between 2200 and 4200 pounds of VDC monomer were contained in the polymers shipped to converters in the past year.

About 85 to 90% of this would be released during the converting process, leaving an estimated 330 to 450 pounds of VDC monomer in the converted product as sold to the final customer.

1.3.6 Market Factors for VDC Polymer End Products

Vinylidene chloride polymers have three properties that make them unique among the various film forming polymers.

(1) Excellent barrier resistance to gases, water vapor, organic vapors and odors.
(2) Flame resistance.
(3) Chemical inertness.

The major markets for VDC polymers are in packaging of foods of all types where preservation of freshness is dependent on maintaining a barrier to oxygen and water vapor.

Since PVDC barrier properties far exceed those of currently used packaging materials, coatings as thin as 1 mil on films with less effective barrier resistance are competitive with most other film constructions made entirely from cheaper, but heavier film.

The market factors for this use are dependent on the product to be packaged and the cost-effectiveness ratio of PVDC film or coated films versus that of other packaging materials. For example, there is no effective shrink wrap film that can compete with Saran or Saran laminates for packaging fresh meats, cheese or frozen poultry. The snack food market is dependent on saran coated packaging films to maintain freshness and package integrity.

In the area of flame resistance, VDC competes with many other products, both organic and inorganic. The basic market factors are cost-performance compared to other materials, durability, and government regulations. Competetion in this area is strong. Unless government requirements for flame retardant textiles or textile products become more stringent, demand for VDC in this area will not be strong.

There are many, less expensive chemically inert materials currently available. Hence use in areas where this property is important will remain limited.

Imports are not a factor in the United States markets. It has been reported that one company, Union Carbide, imports about 3 million pounds of resin annually for film-extrusion. Dow reports exports of about 20 million pounds of VDC polymer products, mostly to Canada, Australia, Latin American and Europe.

1.3.6.1 Extruded Film

Extruded monolayer PVDC film is used as a flexible packaging material for meats, poultry and cheese. Over the past ten years this market has grown steadily at a rate of about 10 percent per year. A recently developed process that can produce a multi-layer sandwich film laminate by combining a 1 mil layer of expensive Saran with heavier layers of less expensive plastic film is tending to supplant the monolayer Saran film. The multi-layer laminate consists of PVDC sandwiched between other plastic films, such as:

Polyethylene - PVDC - Polyethylene
Polyester - PVDC - Polyethylene
Nylon - PVDC - Polyethylene

The laminate uses only one-seventh the weight of PVDC currently required for the monolayer film. One film producer noted that if mono-layer film is phased out in favor of the laminate during the next five years, in which an overall expansion of the flexible film market in the food industry of 5 to 10 percent per year is predicted, demand for PVDC for film over the next five year period will remain fairly static. Once the laminate consumption has stabilized, PVDC demand is predicted to resume its growth rate of 5 to 10 percent over the following five years.

The growth rate for household saran wrap is very small (two to three percent yearly), and is not expected to exceed general population growth. Current publicity concerning the possible hazards of residual VDC in saran wrap* could have a negative impact on the consumer market.

1.3.6.2 Barrier Coatings

The market for flexible film packaging materials in the food industry is highly competitive, and dependent upon a combination of such factors as price, printability, convertability, handling characteristics in packaging machines and in the store, and the ability to preserve the freshness of the stored food. PVDC films (Saran wrap) are expensive, but when used as coating, PVDC imparts its barrier resistant properties to a substrate that is either cheaper or has other desirable physical properties lacking in the PVDC film. Substrates coated with PVDC or saran include:

- Cellophane
- Paper, paperboard and glassine
- Plastic films such as polyethylene, polypropylene, polyester and nylon

During the past six or seven years the saran-coated film market has sustained a growth of about five percent yearly, despite fluctuations in demand for a given coated substrate. Thus, although the PVDC coated paper product market has decreased, this decrease has been offset by significant increases in the coating of polypropylene and polyester films. In the case of cellophane film, we find that although the total volume of cellophane has decreased, the percentage of cellophane coated with PVDC has increased. The net effect in this sector is a relatively constant demand for PVDC. However this demand will tend to decline by 1980.

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*See, for example, Brody, (1977), Chemical Marketing Reporter, (1977) Chem. Eng. News (1977) and Chemical Week (1977).

A slow net growth of PVDC consumption in the food packaging industry should continue over the next five years at a rate of three to five percent annually, mainly attributed to growth in the use of PVDC coated polypropylene and polyester.

1.3.6.3 Specialty Latexes

The market factors affecting VDC consumption in the manufacture of fire retardant latex carpet backing are a combination of economic and legislative considerations. Alumina, PVDC or a mixture of these materials are used to impart flame retardancy to the butadiene-styrene latex backing. Currently, only about 10 percent of flame retardant backing contains PVDC, equivalent to the consumption of seven to eight million pounds VDC monomer.

Growth of this market is slow and not expected to exceed the general expansion rate of the economy. Negative growth impacts could be sustained if the small producers opt to close manufacturing plants rather then expend the capital to reduce emissions during polymerization.* However, PVDC could capture a greater share of the flame retardant rug-backing market if the cost of alumina increased relative to the price of PVDC, or if more stringent federal regulations concerning fire retardancy in rugs and carpets are passed, particularly in the consumer area (current legislation is aimed more at carpet for industrial and commercial use).

1.3.6.4 Textile Fibers

The market growth for modacrylic fibers, made by copolymerizing 10 to 30 percent VDC with acrylonitrile, has been unique in the synthetic textile industry for its slowness. The modacrylics are produced solely for their flame retardant character to satisfy the need for this property in sleepwear, drapery fabric, and automobile upholstery.

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*One company producing VDC copolymers for carpet backing closed one of its two plants for this reason within the past year.

Growth of this market has been impeded by the poor "hand" or physical characteristics of this fiber, the slow development of government regulations concerning flame retardancy for wearing apparel and home furnishings, and the relatively high cost of the fiber. The consumer tends to ignore the potential benefits of flame retardancy, preferring a less expensive and more attractive fabric. The market for modacrylics is expected to sustain slow to moderate growth, about five to eight percent annually.

1.4 TRENDS

Two basic problems were encountered in trying to provide a picture of the VDC production and consumption markets over the past ten years. Vinylidene chloride is manufactured by only two companies, and does not fall under the reporting requirements of the U.S International Trade Commission. Thus, statistics on production are not published in Synthetic Organic Chemicals - U.S. Production and Sales, and must be derived from other data.

Further, sales and volume data on polyvinylidine chloride are not reported separately in the Plastics and Resins Materials section of the above mentioned publication. They are included in the category "Other Vinyl Resins." The footnotes state this category includes polyvinyl butyral, polyvinyl formal, PVDC latex, and PVDC solid and solvent resins. However, the footnotes are not consistent from year to year, and in two years (1973 and 1975) PVDC latex resins are broken out as a separate category. The only end product of VDC for which ITC data is reported is 1,1,1-trichloroethane, and VDC is not the sole raw material from which this product is derived.

Companies polymerizing VDC gave general information on current consumption of PVDC in end use sectors. Interviews with the coating converters yielded little specific information on individual consumption of PVDC in the various end use areas they supplied since they regard this data as highly proprietary. Overall growth data on various packaging materials is published in the Modern Packaging Encyclopedia.

1.4.1 Trends in VDC Production

Based on various published data and industry estimates collected during the course of this study, the amount of VDC produced for the past 10 years has been calculated and is shown in Table 1-4. The VDC production is calculated based on estimates of its consumption in 1,1,1-TCE and VDC copolymers:

(1) VDC Consumption for 1,1,1-TCE Manufacture

These calculations are based on U.S. International Trade Commission (ITC)*reports in Synthetic Organic Chemicals: U.S. Production and Sales, for the production of 1,1,1-TCE and on the approximation (Lowenheim and Moran, 1975) that 30% of 1,1,1-TCE is derived from VDC. The appropriate stoichiometric factors for the reaction were applied.

(2) VDC Consumption in Polymers

VDC polymer production is taken from the Plastics and Resins Materials: U.S. Production Sales section of the Synthetic Organic Chemicals: U.S. Production and Sales (U.S. International Trade Commission). There is an entry reported for "Other Vinyl and Vinylidene Resins." Assumptions were made as to the production of polyvinyl butyral based on estimates of its use in the auto industry (Sczesny, 1977). Assumptions as to the production of polyvinyl formal and other vinyl resins were based on Chemical Marketing Reporter Chemical Profiles on selected resins (see for example, Chemical Marketing Reporter, April 1, 1976.) relating production of various vinyl resins to their raw material sources. The estimated consumption of VDC in the production of polymers over the past 10 years is shown graphically in Figure 1-1.

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*Prior to 1975 this organization was known as U.S. Tariff Commission (TC).

TABLE 1-4. VDC PRODUCTION AND CONSUMPTION TRENDS 1966-1976, MILLIONS OF POUNDS

	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976
Estimated VDC Consumption in Polymers											
a) Based on ITC data*	73	79	84	95	95	n.a.**	90	96	118	143	156
b) Based on SPI data									132	118	143
c) Milgrom, 1976									112		
d) This Report											128***
VDC Consumption for 1,1,1-TCE	53	59	66	71	80	82	97	120	129	100	130
TOTAL VDC CONSUMED****	126	138	150	166	175	n.a.**	187	216	241	243	258
Chemical Intermediate									n.a.**		5.0
Losses											
a) VDC equivalent vented to atmosphere									4.06		1.06
b) VDC equivalent lost as solid polymer									n.a.**		7.8
TOTAL VDC PRODUCED											271.8

*ITC data include U.S. Tariff Commission Data (1966-197 and U.S. International Trade Commission (1973-1976)

**Not available

***This figure does not include polymerization process losses

****Not including losses or uses as chemical intermediate

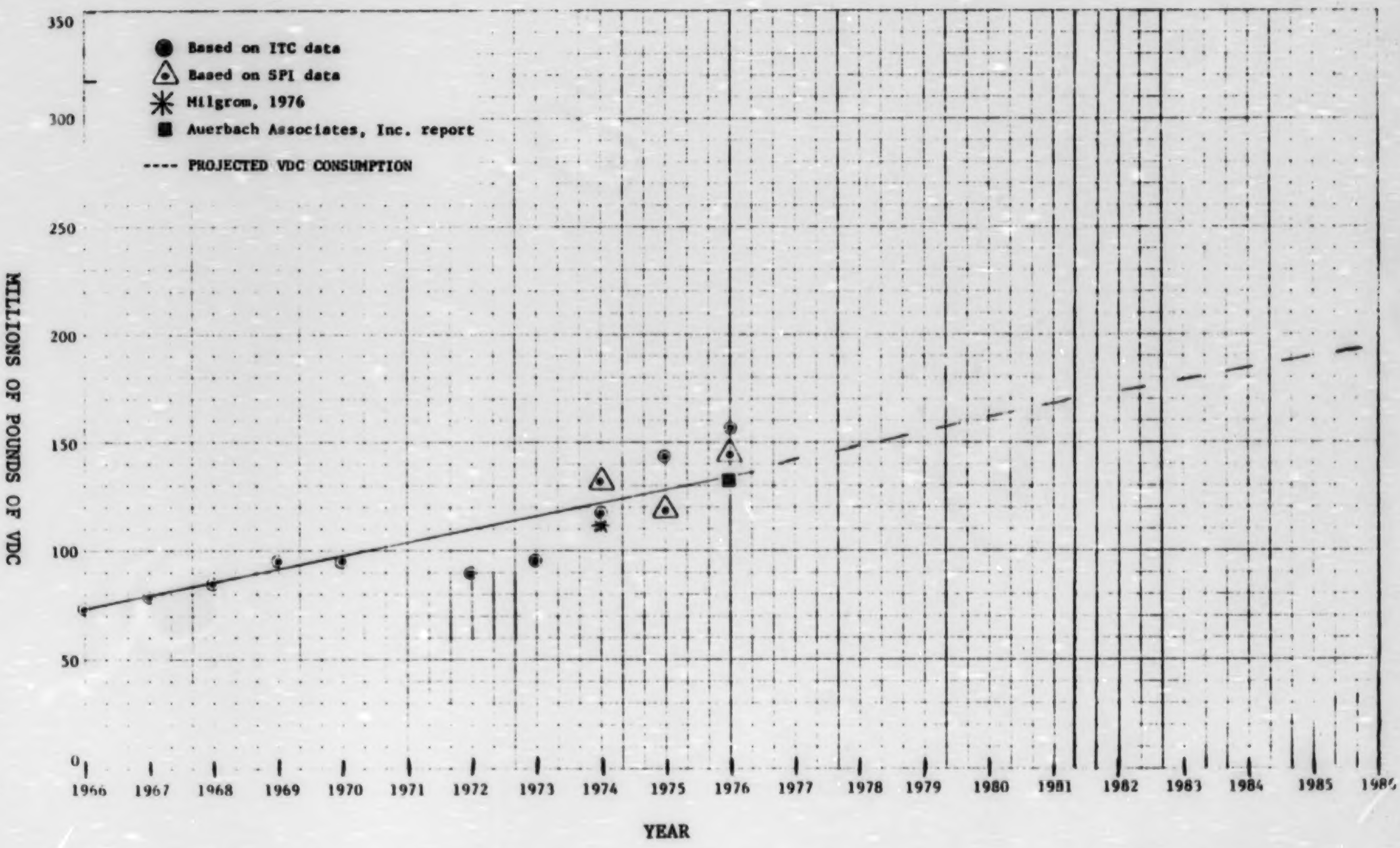

Figure 1-1. Estimated Consumption of VDC in Production of Polymers (U.S.T C 1968, 1969, 1970, 1971, 1972, 1974; U.S.ITC, 1975-1977; SPI, 1974 1975, 1976; Milgrom, 1976, AAI Estimates)

There is some uncertainty with the U.S. ITC data as to exactly what is included in the "other vinyl resins" category, other than polyvinyl formal and butyral. It is possible that this data includes a chlorinated polyvinyl chloride product, Geon, produced by B. F. Goodrich, and having the same formula and molecular weight as PVDC. Further uncertainty arises in the ITC reports' footnotes in the later years (1975 and 1976) which pin point only the formal and butyral resins and omit "other vinyl resins" which are included in the previous years. The ITC itself was unable to clarify this question.

Similarly, some uncertainty as to possible co-reporting of "Other Vinyl Resins" exists in the Society of the Plastics Industry (SPI) data, which would also include Geon in this category. (Society of the Plastics Industry, Inc., 1974, 1975, 1976).*

The estimated total VDC production is arrived at as the sum of its consumption in 1,1,1-TCE and polymers. ITC data was used for all polymer consumption except for 1974, where the figure reported by Milgrom (1976) was taken as being more accurate, and for 1976, where the figure for VDC consumption in polymers calculated for this report was used (132 million pounds). This latter figure is confirmed by PPG's estimate that the 1976 market for VDC polymer products was about 135 million pounds (PPG Industries, 1976).

Trends in VDC consumption for the period 1966-1976 are shown graphically in Figure 1-2. These production estimates are based on calculations of consumption in polymers and in 1,1,1-TCE, and do not include estimates regarding losses, which would increase the production totals. Table 1-4 includes estimates on losses for 1974 (Milgrom, 1976) and 1976 (made during the current study). The VDC emission loss figures for 1976 are much smaller than for previous years due to improvement in both emissions control technology and polymerization process technology.

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*The SPI only includes vinyl butyral and vinyl formal in their "Other Resins" category. This category does not include the modacrylics, and may not include the flame retardant latex for rug backing, depending on how the latex producer reported this data.

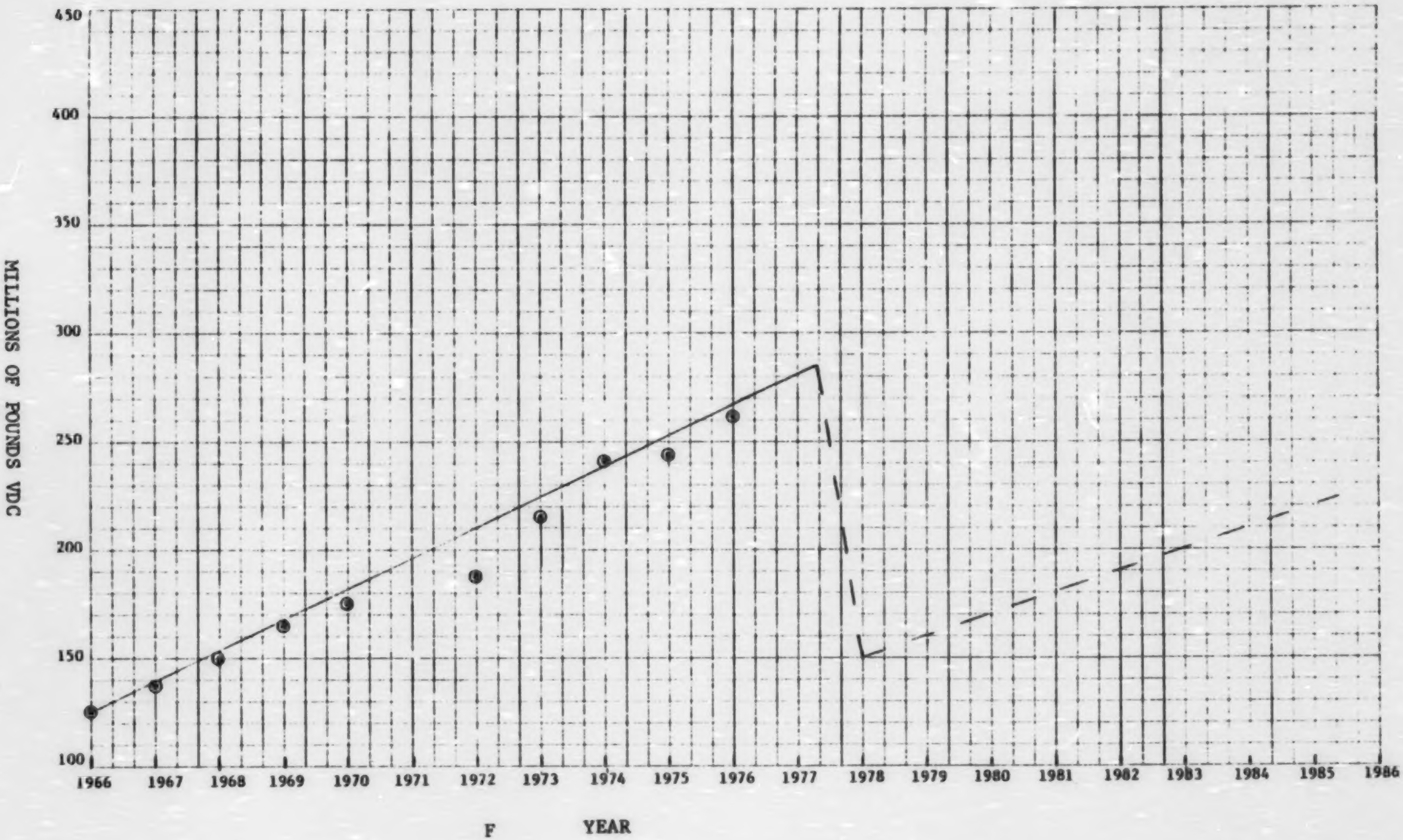

Figure 1-2. Estimated Total Consumption of VDC
(U.S. TC, 1968, 1969, 1970, 1971, 1972, 1974; U.S. ITC, 1975-1977;
SPI, 1974, 1975, 1976; Milgrom, 1976; AAI Estimates).

Further production of VDC is dependent on two major use areas:

1) Polymerization
2) Chemical intermediate, chiefly manufacture of 1,1,1-TCE.

Trends for the growth of VDC consumption in polymer manufacture have been predicted by industry representatives as being 5 to 10% per year for the next 3 to 5 years. PPG's prediction tended to the higher range (7 to 10%) possibly because it included uses of VDC in fiber manufacture and as a flame retardant (PPG, 1976). Other industry sources indicate a somewhat lower growth rate over the next several years of between 5 to 8%. Because of the uncertainties of future economic prospects, including the influence of government regulations and availability of energy and raw material supplies, industry representatives were unable to predict growth trends beyond a 3 to 5 year period.

According to published reports as well as direct confirmation, PPG is expected to discontinue manufacture of 1,1,1-TCE from VDC by 1978. This will decrease VDC consumption by about 130 million pounds per year.

1.4.2 Trends in PVDC Consumption In End Use Markets

The major factor in the growth of PVDC consumption is its application as a barrier material in the production and converting of food packaging materials. As Table 1-5* shows, over 70 percent of the PVDC produced domestically (excluding exports) goes into this industry. This market will thus have the greatest impact on the growth of PVDC consumption.

After many years of continuous growth and relative price stability, flexible packaging materials have entered a period of uncertainty. Following the brief but sudden period of shortages in

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*Polymerizers considered specific polymer production and sales figures proprietary and would not release that data to AAI. Hence end market proportions are calculated on the basis of industry estimates.

TABLE 1-5. PVDC END MARKET PROPORTIONS*
(Industry Sources and AAI Estimates)

MARKET	MILLIONS LBS VDC CONSUMED	% DOMESTIC USAGE	PERCENT OF TOTAL
Flexible Packaging Film	78.5	72.7	61.4
Barrier Coating	21.5	19.9	16.8
Cellophane & Solvent Coating	18.0	16.7	14.1
Extruded Film	39.0	36.1	30.5
Modacrylic Fibers	17.5	16.3	13.7
Carpet Backing	7.9	7.3	6.2
Other Uses	4.0	3.7	3.1
Export	20.0	-	15.6
TOTAL	128.0	100	100

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*Based on VDC consumption and excluding exports

1973 to 1974, and the ensuing price escalation, the volume of these materials declined in 1975 for the first time since prior to 1960.

Since that time, the demand for film packaging materials has resumed and is expected to follow the general economic growth. Safety issues for the consumer concerning monomer migration could both increase federal regulation and decrease consumer demand for specific packaging films (Chemical Marketing Reporter, February 28, 1977.

The greatest growth in the packaging materials market has resulted from the growth of snack food, frozen and prepackaged food and convenience food markets. It is in this specific area that the barrier properties of PVDC find their greatest application. Hence the growth of PVDC consumption will be tied directly to the growth of these markets. Table 1-6 shows the growth of the PVDC packaging film market for the period 1965-1975, in relation to the growth of other packaging materials. Table 1-7 compares the cost of saran and saran-coated substrates with other flexible packaging materials.

As can be seen from Table 1-6, the use of PVDC as a packaging film has been much less than that of polyethylene, vinyl or polypropylene film, despite its superior properties for food storage, remaining steady at about 10 percent annually. The higher cost of PVDC (see Table 1-7), compared to other films or coated substrates, is an important factor in its small share of the market. Because it is more expensive, industry sources predict the growth rate for saran as a household wrap will be slow (two to three percent annually) and parallel growth in the population.

TABLE 1-6. GROWTH OF PACKAGING FILM MARKET (MILLIONS OF POUNDS)
(Modern Packaging Encyclopedia, 1975)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975
PVDC	20	20	20	22	22	22	23	25	25	25	25
Polyethylene	615	730	735	795	895	975	1,100	1,200	1,300	1,375	1,150
Cellophane	405	395	385	360	350	340	330	320	325	335	270
Vinyl	30	40	70	90	105	115	125	135	150	160	150
Polypropylene	40	45	50	65	75	85	90	100	110	115	120
Co-extrusions	-	5	15	20	30	34	40	46	50	55	50
Polystyrene	10	11	12	13	15	15	15	15	15	15	15
Nylon	4	5	5	5	6	7	7	7	7	8	8
Polyester	8	8	8	8	8	8	9	10	12	13	12
Ionomer	-	-	-	-	3	3	4	5	7	9	10
Cellulose acetate	5	5	5	5	5	5	4	3	3	3	3
Phofilm	15	15	10	7	5	3	3	3	3	3	2
Miscellaneous	1	2	3	5	3	3	3	4	4	4	4
TOTAL	1,153	1,281	1,318	1,395	1,522	1,615	1,753	1,873	2,011	2,120	1,819

TABLE 1-7. COMPARATIVE COSTS OF COATED AND UNCOATED SUBSTRATES
(Modern Packaging Encyclopedia, 1975)

COST TABLE: Papers, films, foils*

Material	Cost $/lb.	Cost ¢/1,000 sq. in.
Glassine, Bleached, 25 lb.[1]	$0.44	2.5¢
Lacquered, MS[2], 28 lb.[1]	0.59	3.8
Laminated, amber, 47 lb.[1]	0.48	5.2
Bleached, 47 lb.[1]	0.49	5.4
Waxed, amber, 29/37 lb.[1]	0.42	3.6
Saran coated, 25/30 lb.[1]	0.70	4.8
Pouch paper, Coated, MS, 25, 29 lb.	0.59	4.0
Waxed paper, Bread wrapper, 39 lb.	0.35	3.2
Liner, amber, M[2], 25, 29 lb.	0.45	3.3
Cellophane,		
MS 195	1.08	5.5
MS 220	1.09	4.9
Saran-coated, 140	1.12	8.0
Saran-coated, 195	1.16	5.9
Saran-coated, 250	1.14	4.6
Polyethylene-coated, 182	1.30	7.1
Vinyl-coated, 220	1.13	5.1
Cellulose acetate, Cast, 1 mil	1.25	5.7
Cryovac S, 6/10 mil	1.78	6.5
Fluorohalocarbon, 1 mil	9.26	71.2
Ionomer, 1 mil	0.95	3.2
Nylon, 1 mil	1.43	5.8
Pliofilm, 3/4 mil	1.61	4.9
Polypropylene, Cast[3], 1 mil	0.68	2.2
Balanced, uncoated, 3/4 mil	1.05	2.6
Bal., saran-coated, 0.75 mil	1.40	3.6
Bal., acrylic-coated, 0.84 mil	1.34	3.6
Unbal., uncoated, 0.73 mil	1.05	2.5
Bal., uncoated, 0.90 mil	1.35	4.0
Polystyrene, oriented, 1 mil	1.05	4.0
Polyester,		
Nonheat-sealing, 3/4 mil	1.55	5.8
Nonheat-sealing, 1/2 mil	1.60	3.9
Saran-coated, 3/4 mil base	2.10	8.8
Saran-coated, 1/2 mil base	1.80	5.4

TABLE 1-7. COMPARATIVE COSTS OF COATED AND UNCOATED SUBSTRATES (CONT'D)

Material	Cost $/lb.	Cost ¢/1,000 sq. in.
Polyethylene,		
Low density, 1 mil	$0.50	1.7¢
Medium density, 1 mil	0.51	1.7
High density, 1 mil	0.60	2.1
Heat shrinkable, 1 mil[4]		
Conventional	0.50	1.7
Crosslinked	1.33	4.4
Polyethylene-cellophane, 1 mil/195 MS	1.69	14.6
Polyethylene-polyester, 1 1/2 mil/1/2 mil	1.99	17.2
Saran, 1 mil	1.78	10.9
Vinyl, Cast, 1 mil	0.96	4.2
Extruded, 1 mil	0.71	3.3
Water-soluble film, 1 1/2 mils[5]	1.75	11.7
Aluminum foil, 0.00035 in.	0.86	2.9
0.001 in.	0.69	6.7
Foil-acetate, 0.00035 in./1 mil	2.58	31.0
Labelstock, 0.0003 foil 30 lb. paper	0.57	5.8

---

*Based on reported 1975 prices for representative standard or basic materials and substantial orders. Many other grades, types, gauges, combinations and resulting price variations exist. [1]Based on ream of 500 sheets, 24 by 36 in. or 3,000 sq. feet. [2]MS indicates moistureproof, heat sealing; M is moistureproof. [3]Homopolymer and copolymer grades are offered and range of prices is given to cover various types. [4]Shrink PE films costs range from 50 to 60¢ for heavier gauge pallet wrap. Industrial or bundle-wrap grades are 50¢ and higher. Clarity and other special grades, usually in thinner gauges, are 55¢ and up. [5]This price for polyvinyl alcohol. Other types range up to $4 per pound.

A larger and more rapidly growing sector of the saran film market is in the area of frozen poultry, processed meats, fresh meats, cheese and cookie dough packaging. This sector of the saran film market is predicted to increase at the rate of 10% per year for the next several years and then tend to level off following the economic growth of the country.

A new development in this area is the development of multi-layer laminates in an effort to make this type of barrier film more competitive with other food packaging films. These laminates, consisting of PVDC sandwiched between other plastic films such as polyethylene or polyester, use as little as one-seventh the weight of PVDC as the monolayer film, but provide equivalent barrier properties.

Although the overall food packaging film market is predicted to increase at a rate of about 10% annually, the switch to laminates should result in a static to slow growth rate of PVDC demand for this application over the next five years. Once monolayer film for the food industry is stabilized, the PVDC market is predicted to resume its growth rate of five to ten percent annually (Greenough, 1976).

There are many areas of food packaging where saran film or saran laminates are too costly compared with other packaging materials. However, it would be desirable to impart barrier properties to these cheaper materials. This can be done by coating these with a thin film of PVDC from a latex emulsion.

The growth area for these coated films has been in snack foods which, according to industry estimates, had reached its growth peak of 10% per year several years ago. It is reported that the current rate of growth of this market is on the order of 5% per year.

The trends for saran coating of paper, glassine, paperboard and cellophane are viewed as remaining static or declining, with the major growth predicted for the coating of polypropylene and polyester. Table 1-8 summarizes the trends in market growth for barrier coatings over the next five years.

Overall PVDC consumption growth for coatings is predicted to average between five and ten percent annually, with declines in some areas being offset by greater growth in coating of some plastic films. No new uses for barrier coatings are forseen which would increase the demand. It is anticipated the acrylic coating, particularly on polypropylene, could provide some competition for PVDC coated films.

The entire packaging materials market for food packaging is very competitive. Price is a deciding factor, in most instances, in the selction of the type film or paper product to be used for a given job. Consequently new combinations of film are being developed in an effort to provide the needed protection at the lowest cost. It has been noted (Thiele, 1976), that a major reduction in Saran coating, particularly of paper and glassine could be expected in the next five years as the result of the development of co-extruded polyethylene-polyester film.

TABLE 1-8. PROJECTED GROWTH OF BARRIER COATINGS*

Substrate	Estimated Annual Growth Rate	Comments
Paper, glassine	Zero to decline	Losing out to high density polyethylene, saran coated films, such as cellophane, polypropylene, for snack food packaging
Paperboard	Declining rapidly	Losing out to polyethylene coatings on paperboard
Cellophane	Zero to decline	Losing out to polyethylene, and PVDC coated polypropylene and polyester film
Polypropylene Polyester	10 to 20%	Major growth areas for next five years; then growth predicted to slow to 7 to 10%

---

*Based on interviews with PPG, Grace, FMC, Oscar Meyer and other industry sources

1.5 POTENTIAL IMPACT ON HEALTH AND THE ENVIRONMENT

The flame retardant uses of VDC in polymers, as a modacrylic fiber, or as a comonomer with butadiene-styrene, have had a relatively smaller impact on the total VDC consumption. The growth of this market has been influenced by the relatively high cost of VDC as compared to other flame retardant materials. The effect of government regulations on the use of other flame retardants particularly in the textile field could influence the demand for VDC. A recent example is the banning of TRIS by CPSC and its removal from use in the textile industry. However, it is too early to determine the impact of this regulation on the use of modacrylic fibers as a substitute.

The concentration of VDC monomer in the finished polymer product as used in consumer applications has been reported to be less than 10 ppm and in some cases below 1 ppm. These concentrations are based solely on the monomer concentration related to the PVDC content and do not include the weight of the supporting substrate.

Industry sources reported that there has been a continuing program to reduce monomer concentration in the polymer products to the lowest possible level.

The environmental management of VDC monomer emissions at both manufacturing sites and major polymerization sites has been substantially improved during the past several years. Total emissions have been reduced from that reported by Milgrom (1976) of about four million pounds per year in 1974 to a reported one million pounds per year in 1975-76. The estimated total emissions are shown geographically in Figure 1-3.

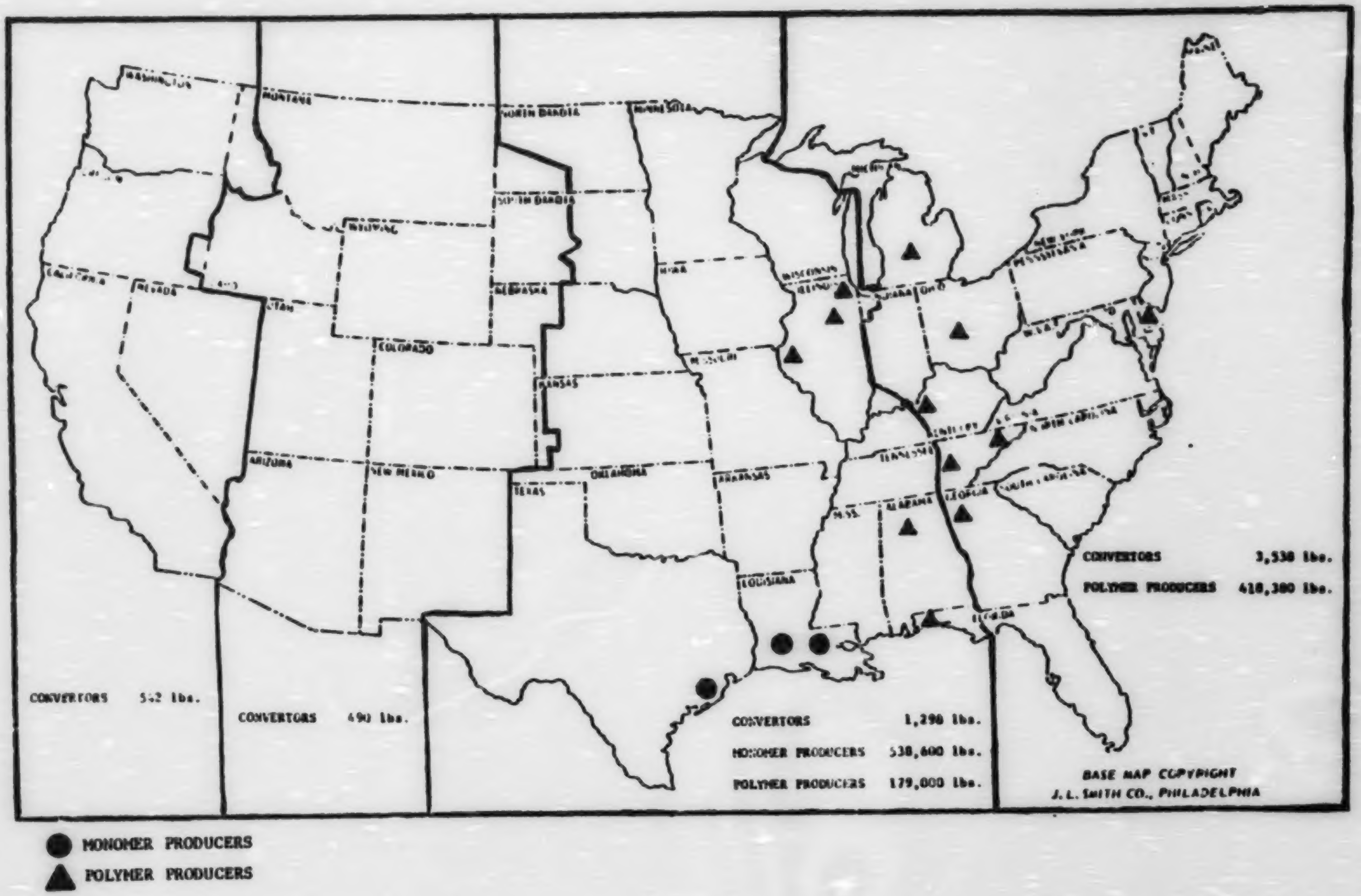
WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WYOMING
CALIFORNIA
NEVADA
UTAH
NEBRASKA
IOWA
WISCONSIN
ILLINOIS
INDIANA
OHIO
NEW YORK
PENNSYLVANIA
COLORADO
KANSAS
MISSOURI
KENTUCKY
NORTH CAROLINA
ARIZONA
NEW MEXICO
OKLAHOMA
ARKANSAS
TENNESSEE
SOUTH CAROLINA
TEXAS
MISS.
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
CONVERTORS 542 lbs.
CONVERTORS 490 lbs.
CONVERTORS 1,290 lbs.
MONOMER PRODUCERS 538,600 lbs.
POLYMER PRODUCERS 179,000 lbs.
CONVERTORS 3,530 lbs.
POLYMER PRODUCERS 418,380 lbs.
BASE MAP COPYRIGHT
J. L. SMITH CO., PHILADELPHIA
● MONOMER PRODUCERS
▲ POLYMER PRODUCERS

Figure 1-3. Estimated Losses for VDC Monomer from all Sources in 1975 (Industry Sources, 1976)

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SECTION II. PHYSICAL AND CHEMICAL PROPERTIES OF VINYLIDENE CHLORIDE, POLYVINYLIDENE CHLORIDE, 1,1,1-TRICHLOROETHANE AND CHLOROACETYL CHLORIDE

2.1 INTRODUCTION

The vinylidene chloride produced in the United States has two basic applications: (1) the synthesis of 1-1,1-trichloroethane, an industrial cleaning agent and (2) the formation, in conjunction with other monomers, of polymers. These polymers are used in the production of flexible packaging materials, as a coating on food packaging materials to improve their barrier resistant properties to oxygen, water vapor and other vapors, as a coating to impart flame resistance to textiles, in the manufacture of flame-resistant textile fibers, and as a comonomer to impart flame resistance to the resulting polymer.

The physical and chemical properties of vinylidene chloride (VDC), 1,1,1-trichloroethane (1,1,1-TCE), and chloroacetyl chloride, a captively used intermediate are presented in this section. Because polymerization is the most important chemical reaction vinylidene chloride undergoes, the physical and chemical properties of its polymer, polyvinylidene chloride are also presented. A bibliography of the pertinent reference sources used to obtain information for this chapter is listed at the end of this section.

2.2 VINYLIDENE CHLORIDE (VDC)

VDC monomer, a di-halogenated, unsaturated hydrocarbon, polymerizes with other monomers to form copolymeric materials. Saran is the generic identifier in the United States for this family of polymers where the VDC content is greater than 50%.

2.2.1 Physical Properties

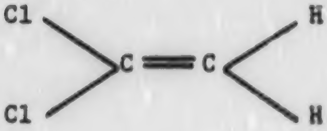
VDC, a colorless liquid with a mild sweet odor, is soluble in most polar and non-polar organic solvents. The monomer forms an azeotrope with 6% methanol. A detailed listing of the physical properties of vinylidene chloride is shown in Table 2-1. Although the values given are for pure vinylidene chloride (1,1-dichloroethylene), they also apply to the commercial product, which is more than 99.6% pure (PPG 1975), and always contains an inhibitor to prevent peroxide formation and subsequent polymerization (see Section 2.2.2).

2.2.2 Chemical Properties and Reactions

In the presence of air or oxygen and at temperatures as low as 40°C, uninhibited vinylidene chloride may form a complex peroxide compound that is violently explosive. The decomposition products of vinylidene chloride peroxides are formaldehyde, phosgene, and hydrochloric acid. The presence of a sharp acid odor thus indicates oxygen exposure and the possible presence of peroxides. Since the peroxide is a polymerization initiator, formation of insoluble polymer in stored vinylidene chloride monomer may also indicate peroxide formation and a potentially hazardous condition. The peroxides are absorbed on the precipitated polymer, and its separation from monomer by filtration, evaporation, or drying may result in an explosive composition. If the peroxide content is more than 15 percent, this solid may detonate from a slight mechanical shock or heat.

VDC residues containing peroxides can be rendered inactive by adding water that is at room temperature, but the hazard may return if the water evaporates. The peroxide can be destroyed by several washes with a 5% by volume solution of methanol in perchloroethylene. Any peroxide present as a component of precipitated polymer in the monomer can be destroyed by

TABLE 2-1. PHYSICAL PROPERTIES OF VINYLIDENE CHLORIDE

Molecular Formula	$CH_2=CCl_2$
Structural Formula	
Molecular Weight	96.95
Physical State	Colorless liquid; mild, sweet odor
Boiling Point @ 760 mm Hg, °C	31.56
Melting Point, °C	- 122.1
Specific Gravity, 20°/20°C	1.213
Refractive Index, n_D at 20°C	1.4249
Viscosity at 20°C, cps	0.330
Vapor Pressure (T°C - mm Hg)	0.0 = 215 20.0 = 495 30.0 = 720 31.8 = 760
Flash Point, °C (Cleveland Open Cup)	- 15
Autoignition Temp. °C	570
Explosive Limits (% by volume in air)	7-16
Latent Heat of Vaporization, 31.8°C, kcal/mole	6.257
Specific Heat, cal/(g)(°C)	0.27
Heat of Formation, kcal/mole	- 6 (liquid monomer)
Heat of Combustion, kcal/mole	261.93
Heat of Polymerization, kcal/mole	18
Solubility of H_2O in monomer at 25°C, wt%	0.25
Solubility of monomer in H_2O at 25"C, wt%	0.035
Dielectric Constant at 16°C	4.67
Beilstein Reference	B1,186

mixing with one part perchlorethylene-methanol solution and four parts VDC monomer.

To prevent formation of peroxide in the monomer, inhibitors are used. The most common is 200 ppm monomethyl ether of hydroquinone (MEHQ). Other inhibitors include alkylamines, phenol, and organic sulfur derivatives. Inhibited VDC is shipped under a nitrogen blanket to avoid contact with air and to prevent the formation of peroxides which can develop very slowly even in the absence of oxygen. (See Section 4.6). To retard polymerization, uninhibited VDC should be kept away from light and at low temperatures, below -10°C. Uninhibited VDC can be stored in mild steel, stainless steel or nickel equipment. Contact with copper, aluminum and their alloys should be avoided as there is danger of acetylide or aluminum chloralkyl formation, which are extremely reactive. Inhibited VDC has indefinite storage life and will not polymerize when kept under a dry blanket of nitrogen with a maximum of 100 ppm oxygen, in the absence of water, light and excessive heat.

VDC vapor is flammable at concentrations between 7% and 16% by volume in air. Vapors of the liquid monomer, once ignited burn strongly but not violently. Vinylidene chloride and hydrochloric acid react to produce 1,1,1-trichloroethane (methyl chloroform) the manufacture of which will be discussed in Section 4.2. The chemical reaction for this process is:

$$CH_2{=}CCl_2 + HCl \longrightarrow CH_3{-}CCl_3$$

There is little information in the literature on the atmospheric degradation of VDC. Recently, Gay et al. (1976) analyzed the products of the photo-oxidation of various chlorinated ethylenes in the presence of nitrogen dioxide with ultraviolet light. Reactivities of the ethylene compounds studied fell in this decreasing order:

VDC $>$ 1,2-dichloroethylene $>$ trichlororethylene $>$ ethylene $\gg$ vinylchloride $>$ tetrachloroethylene

The products of photo-oxidation of VDC were formic acid, hydrochloric acid, carbon monoxide, formaldehyde, ozone, phosgene and chloroacetyl chloride. Chloroacetyl chloride has also been reported as a product from the ozonolysis of VDC (Hull, et al. 1973).

2.3 POLYVINYLIDENE CHLORIDE

Because of the difficulty of fabricating the homopolymer of vinylidene chloride, it has not been used commercially. Wessling and Edwards (1971), give a brief treatment of laboratory polymerization processes for the homopolymer.

Vinylidene chloride copolymerizes with other monomers to form a large number of commercially useful copolymers and terpolymers as shown in Tables 2-2 and 2-3. These polymers contain more than 50% VDC, and are used primarily to produce films with excellent barrier properties or to produce latexes for coatings on other materials. The commercially important comonomers used with VDC are vinyl chloride, acrylonitrile, and alkyl acrylates. Many commercial saran polymers contain three or more components, vinylidene chloride being the major one. Usually one component is introduced to improve the processability or solubility of the polymer, and others are added to modify specific end-use properties.

VDC is also copolymerized with other monomers where the amount of VDC present is less than 50%. In this case, it is used as an adjunct to improve the fire-retardancy of the major monomer in the polymer. Examples of this use are in the production of modacrylic fiber, where VDC is copolymerized with acrylonitrile, and as a latex backing for carpets, where the major polymer is styrene-butadiene.

2.3.1 Physical Properties

Generally, VDC copolymers are odorless, tasteless, non-toxic, and flame-retardant. They show toughness and abrasion resistance. Oriented filaments, fibers and films have tensile strengths of between 8,000-60,000 psi, depending on composition and the degree of orientation. Physical

TABLE 2-2. COMPOUNDS FORMING COPOLYMERS WITH VINYLIDENE CHLORIDE[a] (EXCLUDING VINYL CHLORIDE)

(Gabbett and Smith, 1964)

Type

Aromatic Compounds

Allyl carbonate derivatives of aromatic hydroxy esters
Diallyl phthalate
Diesters of tetrahydro-*endo*methylene phthalic acid
9-Methylene fluorene
3-Methylene phthalide
Styrene and derivatives

Heterocyclic Compounds

N-Isopropenyl derivatives of 2-oxazinones and 2-oxazolidinones
N-2-Norcamphanyl acrylamides
Vinylfuran
Vinyl oxazolidinone

Miscellaneous Compounds

Acrylonitrile

Aliphatic epoxides
Alkenyl silanes
Allyl-3,4-epoxy-2-hydroxybutyrate
Allyl esters of dicarboxylic acids
Butadienes
1,1-Dichloro-1,3-butadiene
N-Fluoroalkyl-N-vinyl amides
N-Hydroxymethyl maleimide
Isopropenyl isocyanate
β-Methylene-β-propiolactone
2,4,6-Trially-1,3,5-tricyclohexylborazine
2,4,6-Trivinyl-1,3,5-tricylohexylborazine
Unsaturated esters of halo derivates of acetic acid
Unsaturated ketones
Vinyl compounds (general)
Vinyl isocyanate
Vinylidene cyanide

Type

Olefinic Compounds

Chlorotrifluorethylene
Ethylene
Fluoroprene
Isobutylene

Haloolefins (general)
Olefins (general)
Tetrafluoroethylene
3,3,3-Trifluoropropene

Unsaturated Acids & Esters

Alkyl acrylates

Alkyl methacrylates
Allyl acrylate
Diamidophosphoroacrylates
Ethyl fumarate
Methyl 2-chloroacrylate
Sodium sulfopropyl arylate
Trialkyl aconitates
Vinyl isothiocyanate

Vinyl Esters

Butyl vinyl sulfonate
Vinyl acetate
Vinyl 3-alkoxybutyrates
Vinyl esters of carboxylic acids (general)

Vinyl Ethers

Dodecyl vinyl ether
Trifluoroethyl vinyl ether

a - Copolymers containing at least 50% VDC.

TABLE 2-3. COMPOUNDS FORMING TERPOLYMERS WITH VINYLIDENE CHLORIDE[a]

(Gabbett and Smith. 1964)

Second Monomer	Third Monomer
Acrylates or acrylonitrile	Isopropenyl acetate
Acrylic or methacrylic acid	Vinyl or acrylate esters
Acrylonitrile	Butadiene
	Methyl methacrylate
	α-Methylstyrene
	Vinylidene chloride
	5-Vinyl-2-picoline
α-Alkyl acrylates	Vinyl chloride
Alkyl maleates	Vinyl esters
Allyl chloride	Diallyl fumarate
1,3-Butadiene	Chloroprene
Butadiene	Ethyl acrylate
	Isobutylene
	Methyl methacrylate
	α-Methylstyrene
	Styrene
	Vinyl acetate
	Vinyl chloride
	Vinyl compounds
N-2-Formamidoethylacrylamide	Vinyl chloride
Isobutylene	Polymerizable substances
1-Chloro-1-bromoethylene	Vinylidene bromide
Glycidyl methacrylate	(2-Methacryloyloxyethyl) diethyl ammonium methyl sulfate
Methyl acrylate	Trichloroethylene
	Vinyl chloride
Styrene	Vinyl chloride
Vinyl halides	Acrylic or methacrylic compounds
	Tetrapolymer
Acrylic acid	Acrylonitrile Methyl methacrylate

---

[a] Limited to those copolymers containing at least 50% vinylidene chloride.

properties of polyvinylidene chloride* are summarized in Table 2-4.

2.3.1.1 Structure

The chemical composition of polyvinylidene chloride homopolymer has been confirmed by various techniques including elemental analysis, x-ray diffraction analysis, infrared, Raman, and NMR spectroscopy and degradation studies. The polymer chain is made up of vinylidene chloride monomer units added head to tail.

$$-CH_2-CCl_2-CH_2-CCl_2-CH_2-CCl_2-$$

Since the repeat unit is symmetrical, no possibility exists for stereoisomerism. The chain structure of PVDC homopolymer is shown in Figure 2-1. Although the chemical composition of the PVDC homopolymer chain is well-established, almost nothing is known about its size or size distribution. No direct measurements of molecular weight have been reported in the literature (Wessling and Edwards, 1967).

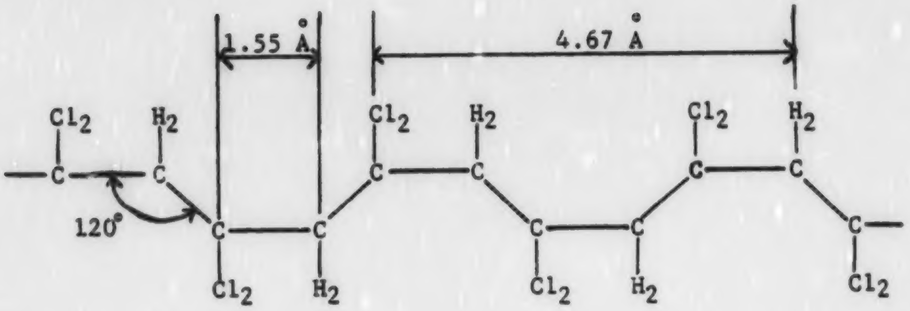


Figure 2-1. Chain Structure of Polyvinylidene Chloride Homopolymer (Gabbett and Smith, 1964)

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*Unless stated otherwise, the use of the term polyvinylidene chloride (PVDC) in this section refers to the copolymerized form of vinylidene chloride and not to the homopolymer.

TABLE 2-4. PROPERTIES OF POLYVINYLIDENE CHLORIDE HOMOPOLYMER

(Dean, 1973; Brandup and Immergut, 1975)

Physical	
Specific gravity	1.65 - 1.72
Specific volume, cu. in./lb.	16-17
Coefficient thermal expansion, linear x 10^5	19
Specific heat, cal/g.	0.32
Thermal conductivity x 10^4	2.2
Heat capacity kJ/kg °K	0.857
Heat distortion temperature, °F	150-180
Heat resistance - continuous, °F	160-200
Flammability, in/min.	none
Water absorption, % ASTM D-570 after 24 hours	0.8-1.2
Glass transition temp. T_g (°K)	255
Refractive index n_D at 20° C	1.60-1.63
Critical surface tension$^{20°C}$ (mNm^{-1}) = ($dyn\ cm^{-1}$)	40
Mechanical	
Impact strength, Izod ft-lbs.in.	0.3-1.0
Tensile strength, ASTM D-638 (mPa)	
Elongation at break, ASTM D-638	High=250
Flexural strength, ASTM D-790 (mPa)	29-43
Compressive strength, psi x 10^{-3}	4.5-5.5
Hardness, ASTM D-785, ASTM D-1706	M50-M65
Electrical	
Volume resistivity ASTM D-257 (Ohm.cm)	$1.0 \times 10^{14} - 1.0 \times 10^{16}$
Dielectric strength, short time, ASTM D-149 (Vcm^{-1}).10^{-3} to convert to volts/mil., multiply by 2.54	160-240
Dielectric constant, ASTM D-150 at 60 Hz	4.5-6.0
Dissipation factor, ASTM D-150 at 60 Hz	0.03-0.045
Fabrication	
Bulk factor	2
Injection molding temp., °F	300-400
Injection molding, pressure, psi x 10^{-3}	10-30
Mold shrinkage, mils/in.	5-15

Variation may occur in these values since the properties of a molded article depend not only on the plastic used but on many other factors including conditions of forming and design of the molded part itself.

2.3.1.2 Crystallinity

The homopolymer of vinlyidene chloride and copolymers comprised principally of vinylidene chloride show a strong tendency to crystallize, have high softening temperatures and relatively sharp melting points. Copolymers containing more than about 15 mole % acrylate or methacrylate are amorphous. Substantially more acrylonitrile, (~25 mole %), or vinyl chloride, (~45 Mole %), is required to destroy crystallinity.

The more common crystalline copolymers show their maximum rates of crystallization in the range of 80-120°C. In many cases, these have broad composition distributions containing both polymer unit fractions of high vinylidene chloride content which crystallize rapidly, and other polymer units that do not crystallize at all. The copolymers may remain amorphous for considerable periods of time if quenched to room temperature. The induction time before the onset of crystallization depends on both the type and amount of comonomer; the homopolymer crystallizes within minutes at 25°C. Orientation or mechanical working accelerates crystallization and has a pronounced effect on morphology. Crystallographic data for PVDC homopolymer is given in Table 2-5.

Because VDC polymers are, in comparison with other polymers, impermeable to a wide variety of gases and liquids, they exhibit barrier properties which make them commercially important. Their impermeability is a consequence of the combination of high density and high crystallinity in the polymer. An increase in either tends to reduce permeability though a more subtle factor may be the symmetry of the polymer structure. PVDC has an unusually low permeability to H_2O as is shown in Table 2-6.

Table 2-7 gives the permeability of PVDC to a variety of gases. Permeability is affected by both kind and amount of comonomer as well as by crystallinity.

2.3.1.3 Solubility

PVDC does not dissolve in most common solvents at ambient temperatures. This is due less to its polarity than its high melting point. It dissolves readily in a wide variety of solvents at temperatures above 130°C (Wessling, 1970). Various solvents for PVDC are shown in Table 2-8.

TABLE 2-5. CRYSTALLOGRAPHIC DATA FOR PVDC HOMOPOLYMER

(Brandup and Immergut, 1975)

CRYSTAL	SPACE	UNIT	CELL	PARAMETERS		MONOMERS/ UNIT	DENSITY$^{g/cc}$	
System	Group	A	B	C	Angles	Cell	Crystal	Amorph
Mono		22.54	4.68	12.53	B=84.2	16	1.958	
"	C2-2	6.73	"	12.54	B=123.6	4	1.957	
"		13.69	4.67	6.296	B=55.2	4	1.948	
								1.66
								1.7754

Mono = monoclinic

A, B, C = angstroms

Angles α and δ are 90°. β (B) is given in Table.

Monomers/unit cell: no. of base units in cell unit

TABLE 2-6. COMPARISON OF THE PERMEABILITIES OF VARIOUS POLYMERS TO WATER VAPOR (Wessling and Edwards, 1967)

Polymer	Density, g/ml amorphous	Density, g/ml crystalline	Permeability[a] amorphous	Permeability[a] crystalline
ethylene	0.85	1.00	200-220	10-40
propylene	0.85	0.94	420	
isobutylene	0.915	0.94	90	
vinylchloride	1.41	1.52	300	90-115
vinylidene chloride	1.77	1.96	30	4-6

[a] In g/(hr) (100 in.^{2}) at 53 mm Hg pressure differential and 39.5°C for a film 1 mil thick.

TABLE 2-7. PERMEABILITY COEFFICIENTS FOR PVDC

(Brandup and Immergut, 1975)

Permeant	T(°C)	$P \times 10^{10}$	Ep kj/mole
He	34	0.31	
N_2	30	0.00094	70.2
O_2	30	0.0053	66.5
CO_2	30	0.03	51.4
H_2O	25	0.5	46.0
H_2S	30	0.03	74.4

$$\underset{\text{(rate of transmission)}}{P} = \frac{\text{(amount of permeant) (film thickness)}}{\text{(area) (time) (pressure - drop across the film)}}$$

Units of P: cm^3 (STP)-cm/cm^2-sec-cmHg

Ep: activation energy of permeation

TABLE 2-8. SOLVENTS FOR POLYVINYLIDENE CHLORIDE
(Wessling and Edwards, 1967)

Solvents	Tm, °C[a]
nonpolar	
1,3-dibromopropane	126
bromobenzene	129
α-chloronaphthalene	134
2-methylnaphthalene	134
o-dichlorobenzene	135
polar aprotic	
hexamethylphosphoramide	-7.2
tetramethylene sulfoxide, TMSO	28
N-acetylpiperidine	34
N-methylpyrrolidone	42
N-formylhexamethylenimine	44
trimethylene sulfide	74
N-n-butylpyrrolidone	75
isopropyl sulfoxide	79
N-formylpiperidine	80
N-acetylpyrrolidine	86
tetrahydrothiophene	87
N,N-dimethylacetamide	87
cyclooctanone	90
cycloheptanone	96
n-butyl sulfoxide	98

[a] Temperature at which a 1% mixture of polymer in solvent becomes homogeneous.

Copolymers with a high enough vinylidene chloride content to be quite crystalline, behave much like PVDC homopolymer. They are more soluble, however, because of their lower melting points. The solubility of amorphous copolymers is much higher. The selection of solvents, in either case, varies somewhat with the type of comonomer. Solvents that dissolve the homopolymer also dissolve the copolymers, but at lower temperatures. Solution properties of PVDC homopolymers have not been studied in detail.

2.3.1.4 Migration of Monomer from Polymer

Since VDC polymer finds many applications in the food industry as a packaging material, it is of interest to know whether traces of unreacted monomer trapped in the polymer will migrate out into the contacted substance. During the past year the Indirect Additives Laboratory of the Food and Drug Administration has been conducting a study on the migration of various monomers in plastics into foods. They have developed measurement methods for analyzing both vinyl chloride and vinylidene chloride in food simulants (water, heptane and corn oil). The studies consisted of placing plastic films in contact with food simulants, and measuring the migration as a function of time and temperature. Preliminary findings indicate that VDC monomer does migrate from the polymer (Breder, 1977). Results are to be published in the Journal of the Association of Official Analytical Chemists in the coming year.

However, Dow researchers have stated that studies of foods wrapped in plastics made from VDC had showed that none of the chemical migrated from the wrapping to the food.* The tests would have disclosed such contamination if the VDC concentration exceeded 10 ppb. (New York Times, February 23, 1977, Chemical and Engineering News, February 28, 1977). These reports have been confirmed by Dow spokesmen (Wintermyer, 1977).

2.3.2 Chemical Reactions

2.3.2.1 Thermal Decomposition

PVDC begins to decompose at about 125°C. In the very early stages of thermal decomposition (<1%), PVDC discolors and becomes insoluble. A gradual rise in temperature causes conjugated double bonds to appear, after which the polymer becomes infusible, the crystal structure is destroyed, aromatic structures form, and finally, graphitization occurs (Wessling and Edwards, 1967). Upon incineration PVDC completely breaks down with no intermediate oxychlorinated products formed. (PPG, 1976).

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*These tests were FDA recognized extraction studies from food wrap materials in food simulated solvents.

The basic degradation reaction of PVDC is:

1. Formation of a conjugated polyene

$$\left(CH_2CCl_2 \right)_n \xrightarrow{fast} \left(CH{=}CCl \right)_n + nHCl$$

2. Carbonization

$$\left(CH{-}CCl \right)_n \xrightarrow{slow} 2n\,C + nHCl$$

Heat, ultraviolet and ionizing radiation alkaline reagents, and catalytic metals or salts can effect the process. The common feature of these reactions is that chlorine is removed from the polymer, either as chloride ion or hydrogen chloride depending on the medium.

2.3.2.2 Photodegradation

PVDC does not appear to degrade at a measurable rate in the dark at temperatures below 100°C. When exposed to ultraviolet radiation (uv) or sunlight, it discolors. Hydrogen chloride is eliminated in the process and crosslinking takes place. An interesting aspect of a study by Oster et al. (1962) on photodegradation reactions was that a photoconducting plastic can be produced by the ultraviolet irradiation of PVDC film.

Unlike UV, higher energy irradiation (gamma rays) of PVDC causes chain scission. Copolymers of VDC and VC undergo both crosslinking and chain scission. The relative amounts of the two reactions are a function of VDC content in the copolymer (Tsuchida, et al., 1964). A higher proportion of VDC produces more scission than crosslinking. Crosslinking is increased at elevated temperatures during irradiation, and decreased in the presence of oxygen. However, a much larger effect is exerted by the physical form or heat history of the solid copolymer itself. Based on changes in viscosity of vinylidene chloride/vinyl chloride copolymer material, it has been shown that molded sheet specimens evince more crosslinking than unfabricated molding powder (Harmer and Raab, 1961).

2.3.2.3 Alkaline Decomposition

While the mechanism for alkaline decomposition is not known, it is clearly an ionic reaction whose final products are carbon and chloride ion. The reaction is very fast and is effected by strong bases such as alcoholic KOH, metal alkyls, active metals and others. The rate is based on surface area since PVDC is not soluble in the solvents used for alkaline decomposition. Weak bases, such as ammonia or amines, accelerate the decomposition but do not produce a simple polyene product. Aqueous solutions have a limited effect on PVDC because of the relative insolubility in water. However, PVDC can be decomposed by hot concentrated caustic over a period of time, but decomposition products do not have a simple polyene structure (Wessling and Edwards, 1967).

2.3.2.4 Catalytic Decomposition

Various metal salts such as $FeCl_3$, $AlCl_3$, and $ZnCl_2$ catalyze the thermal decomposition of PVDC. This problem is of great practical importance because Saran polymers, when heated, release hydrogen chloride. If they are in contact with a metal surface, the metal chloride forms and catalyzes further decomposition, thereby greatly accelerating the reaction. As a consequence, attempts to extrude unstablized saran in conventional steel equipment lead to almost explosive decomposition. Very little is known about the mechanism of the reactions; the major industrial emphasis has been on preventative measures. Metal parts intended to be used with saran are fabricated from acid-resistant alloys or nickel. Nickel salts are much less active as catalysts. In addition, the polymers are usually stabilized with some type of metal-ion scavenger (Wessling and Edwards, 1967).

2.3.2.5 Stabilization of PVDC

Since exposure of polymers to heat, ultraviolet light, oxygen and metals is unavoidable in most applications, both during processing and service life, these effects must be minimized by the addition of stabilizers during compounding to insure a reasonable service life for the material. An ideal stabilizer system should include: (1) an acid acceptor which will combine with HCl but not strip it from the polymer, (2) an ultraviolet absorber which prevents conjugation from occuring and breaks up discoloration due to the conjugation, (3) an antioxidant to prevent formation of carbonyl groups and other chloride scavengers, and (4) chelating agents to prevent metal chloride formation which accelerates PVDC degradation. The stabilizers are usually used in combinations and frequently produce synergistic effects (Wessling and Edwards, 1967). Specific examples of the various stabilizers can be found in the literature (Wessling and Edwards, 1967; Chevassus and de Broutelles, 1963; Platzer, 1967; Thacker, 1971-1972; Gross, 1974-1975).

2.4 1,1,1-TRICHLOROETHANE (METHYL CHLOROFORM)*

Besides the formation of VDC polymers, vinylidene chloride finds commercial use in the manufacture of 1,1,1-trichloroethane, (1,1,1-TCE). At the present time, only one manufacturer (PPG Industries) produces 1,1,1-TCE from vinylidene chloride. The most widespread application of 1,1,1-TCE is as a cold solvent used in the cleaning and degreasing of metals and other items. In addition, the chemical is used as a vapor pressure depressant in the aerosol industry and in the formulations of such products as adhesives, cutting oils, and non-flammable paints.

2.4.1 Physical Properties

1,1,1-TCE is noncorrosive to common metals, is non-flammable, possesses no flash point or fire point and is one of the least toxic chlorinated hydrocarbons. For commercial purposes, methyl chloroform is stabilized or inhibited to prevent hydrolysis. A summary of physical properties for 1,1,1-TCE, both inhibited and uninhibited, is presented in Table 2-9. As is shown by this Table, the properties of the stablized material differ little from the unstabilized form.

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*The names 1,1,1-trichloroethane and methyl chloroform are used interchangeably in the literature.

2.4.2 Grades

Grades of methyl chloroform are manufactured according to their end-use. The small differences in properties among the various grades are due to different types or concentrations of inhibitor; the purity of the methyl chloroform is the same for all grades. The inhibitor may affect the specific properties and uses of the solvent. These compounds are considered proprietary by the manufacturers. Typical inhibitors which have been reported are discussed in Section 2.4.3.3.

Table 2-10 shows specifications and typical analyses for two grades of methyl chloroform, one used for cold cleaning, aerosol formulations and vapor degreasing, and the other grade, which contains less inhibitors used for adhesives, and film processing and various syntheses.

2.4.3 Chemical Reactions

2.4.3.1 Thermal Decomposition

Different decomposition products result from heating methyl chloroform under varying conditions.

Heated at 75-160°C, at elevated pressure and in the presence of sulfuric acid or metal chlorides, and depending on the quantity of water present 1,1,1-TCE forms acetyl chloride, acetic acid or acetic anhydride. At temperatures up to 370°C, 1,1,1-TCE is one of the more stable chlorinated aliphatic solvents with respect to phosgene formation. However, at temperatures above 700°C or when exposed to open flames or electrical elements, uninhibited 1,1,1-TCE is subject to atmospheric oxidation, yielding phosgene, carbon monoxide, carbon dioxide, hydrogen chloride and water (The Franklin Institute, 1975).

TABLE 2-9. PHYSICAL PROPERTIES OF 1,1,1-TRICHCLOROETHANE UNINHIBITED AND INHIBITED GRADES*

(PPG Industries, 1968)

Physical Properties	Uninhibited Grade	Inhibited Grade
Chemical Formula	CH_3CCl_3	CH_3CCl_3
Physical State	liquid	liquid
Color	clear, water white	clear, water white
Odor	mild, chloroform-like	mild, chloroform-like
Boiling Range	74.1°C (165.2°F)	70-88°C (158-190°F)
Melting Point	-30.41°C	
Specific Gravity @25/25°C	1.336	1.288-1.321
Refractive Index$_{nd}$20	1.4379	
Explosive Limits	flammable at elevated temperatures and pressures	
Autoignition Temperature	500°C(932°F)	
Deliquescence	no	no
Density at 25°C	1.332	1.284-1.317
Dielectric Constant	5.007$^{(34.9°C)}$	
Hygroscopicity	no	no
Light Sensitivity	no	no
Flash Point	none	none
Tolerance	350 ppm in air	
Specific Heat	0.25 cal /gm /°C	0.25 cal /gm /°C
Vapor Density (Air =1)	4.55	4.55
Vapor Pressure @30°C	144 mg Hg	144 mg Hg
Viscosity @25°C	0.59 Centistokes	0.61 Centistokes
Surface Tension, 20°C, dyn/cm.	25.56	
Solubility of 1,1,1 TCE in water	0.44 g/100g	
Solubility of Water in 1,1,1 TCE	0.05 g/100 g	
Solubility (room temp.) in: alcohol ether	soluble in all proportions	

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* Blank spaces indicate lack of available data for that property.

TABLE 2-10. SPECIFICATIONS AND TYPICAL ANALYSES FOR TWO GRADES OF 1,1,1-TRICHLOROETHANE (METHYL CHLOROFORM) (PPG, 1968)

	INHIBITED METHYL CHLOROFORM (VAPOR DEGREASING & AEROSOL GRADE)		LOW-STABILIZED METHYL CHLOROFORM (SPECIAL ADHESIVES GRADE)	
PROPERTY	SPECIFICATION	TYPICAL	SPECIFICATION	TYPICAL
Appearance	Clear, water white	Passes	Clear, free of suspended matter	Passes
Color, APHA	15 maximum	7	15	7
Specific Gravity, 25°/25°C	1.300-1.320		1.320-1.336	1.333
Distillation Range (100%), °C	72.0-88.0	73.0-83.3	70-79	74.1-75.5
Acidity, as HCl, %	0.0010 maximum	0.0002	0.001 maximum	0.0003
Aluminum Corrosion (Reflux)	no effect on solvent or aluminum	Passes		
Water Content, PPM	100 maximum	65	100	50
Non-Volatile, % by wt.	0.0010 maximum	0.0002	0.001	0.0005
Methyl Chloroform, % (Minimum)			99.0	99.6

$$3CH_3CCl_3 + 5O_2 \xrightarrow{700^\circ C} 5HCl + 2CO_2 + 2CO + 2COCl_2 + {}^{2}H_2O$$

2.4.3.2 Corrosion

When dry, uninhibited methyl chloroform has little effect on common construction materials. However, in the presence of any traces of moisture, corrosion occurs due to the formation of hydrogen chloride. The inhibited or stabilized grade does not corrode any common metal used commercially, including aluminum, brass, cooper, iron, monel, steel, tin and zinc at temperatures up to 79.4°C (175°F) (Manufacturing Chemists' Association, 1976).

The low stabilized grade, however, may corrode common commercial metals, with the exception of stainless steel.

2.4.3.3 Stabilization

Although 1,1,1-TCE is substantially more stable to oxidation than other chlorinated hydrocarbons, significant amounts (3-8%) of stabilizing substances are always added to prevent thermal decomposition or hydrolysis. Representative stabilizers are reported to be nitromethane, N-methylpyrrole, 1,4-dioxane, butylene oxide and 1,3-dioxolane (Lowenheim and Moran, 1975).

2.4.3.4 Reactions with Alkaline Materials

Methyl chloroform reacts with a solution of sodium hydroxide to yield vinylidene chloride. This reaction is the basis for commercial production of VDC. In the presence of strong alkalies such as caustic soda, flammable or explosive products may be formed. (PPG, 1968).

2.4.3.5 Other Reactions

Methyl chloroform forms an azeotrope with methanol (21.7%) boiling at 56°C. In the presence of chlorine and sunlight, 1,1,1,2-

tetrachloroethane and small quantities of penta- and hexachloroethane are formed. Reaction with anhydrous hydrogen fluoride at 144°C in the absence of a catalyst results in the formation of 1,1-dichloro-1-fluoroethane and 1-chloro-1,1-difluoroethane.

2.5 CHLOROACETYL CHLORIDE

Chloroacetyl chloride is of only marginal interest to the present study. It is produced by Dow from vinylidene chloride. Dow produces about 5 million pounds per year for captive use as an intermediate for other syntheses.

Chloroacetyl chloride has also been used in the production of chloroacetophenone, the principal ingredient of the riot control gas MACE.

2.5.1 Physical Properties

Chloroacetyl chloride is a non-flammable liquid, highly corrosive to metal and skin. A summary of its physical properties is presented in Table 2-11.

2.5.2 Chemical Reactions

There are two chemical reactions of chloroacetyl chloride of interest to this study. Its decomposition in water liberates the monochloracetic acid and HCl, which accounts for its lachrymatory effect on the eyes and its corrosiveness to metals.

$$ClCH_2COCl + H_2O \longrightarrow HCl + ClCH_2COOH$$

In the presence of benzene and an aluminum chloride catalyst, it can be used to prepare omega-chloroacetophenone, the principal ingredient in tear gas or MACE.

$$ClCH_2COCl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCH_2Cl + HCl$$

TABLE 2-11. PHYSICAL PROPERTIES OF CHLOROACETYL CHLORIDE

Formula:	$ClCH_2COCl$
Molecular weight:	112.95
Physical State:	Liquid
Color:	Clear, water-white
Odor:	Very pungent
Boiling Point @760 mm Hg.	107°C
Freezing Point	-21.77°C
Specific Gravity @ 0°C	1.495
Refractive Index n_D^{20}	1.4541
Density, d_4^{20}	1.4202
Beilstein Ref.	2,199
Solubility:	
in water	Decomposes
in alcohol	Decomposes
in acetone	Soluble
in ether	Soluble in all proportion

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SECTION III. MANUFACTURING PROCESS STUDY

3.1 PRESENT STATUS OF THE INDUSTRY

Vinylidene chloride (VDC) is one of a number of chemicals obtained by the chlorination of ethylene or ethane. VDC, like vinyl chloride, contains a double bond that enables it to be polymerized into a long chain compound.

Polymers of pure vinylidene chloride form a crystalline structure that have found little if any commercial application. When copolymerized with other double bond containing monomers such as vinyl chloride, butadiene, styrene, or acrylonitrile, VDC forms polymeric compounds that are used as a barrier coating on paper and other plastic films, to produce a tough, flexible film; as a textile fiber with flame retardant properties and resistance to many chemicals; and as a flame retardant elastomer.

The copolymers of vinylidene chloride have not found the large market enjoyed by vinyl chloride, styrene, acrylonitrile-butadiene-styrene (ABS), or polyethylene because, on a cost-performance basis they are more expensive, or they do not possess the physical properties of the competing polymers.

At present, two companies manufacture vinylidene chloride monomer: Dow Chemical Company and PPG Industries, Inc. Over the years one other company has manufactured VDC, but, generally for economic reasons, ceased production. Vulcan Materials Company produced VDC from late 1970 to January 1974.

Dow Chemical Company makes VDC monomer chiefly for captive use. A portion of its production (industry estimates about 15 to 20%), enters the merchant market. PPG Industries, Inc. manufactures VDC monomer chiefly as an intermediate for the synthesis of 1,1,1-trichloroethane (1,1,1-TCE) or methyl chloroform. It is estimated that 80% of PPG's present production is used in the synthesis of 1,1,1-TCE, the balance enters the VDC merchant market.

Substantially all the VDC sold in the merchant market is used by approximately 12 companies to manufacture a variety of copolymers.

PPG's initial interest in producing vinylidene chloride was developed from its desire to produce 1,1,1-trichloroethane by direct hydrochlorination of vinylidene chloride, using the process indicated by equations (1a), (1b) and (1c). It has been reported within the past year that PPG is expanding its production of 1,1,1-trichloroethane. However, it has been stated that the plant expansion will be based on the use of a new process that will not require the intermediate formation of vinylidene chloride.

Dow's probable interest in both 1,1,1-trichloroethane and vinylidene chloride production developed from its major position as a producer of vinyl chloride and other chlorinated hydrocarbons. Vinylidene chloride became a cost-effective addition to the product mix using the route suggested by equations (2a), (2b), and (2c).

(1a) $CH_2Cl-CH_2Cl + Cl_2 \longrightarrow CH_2Cl - CHCl_2 + HCl$
1,1,2-Trichloroethane

(1b) $CH_2Cl - CHCl_2 + NaOH \longrightarrow CH_2 = CCl_2 + NaCl + H_2O$
Vinylidene Chloride

(1c) $CH_2 = CCl_2 + HCl \longrightarrow CH_3 - CCl_3$
1,1,1-Trichloroethane

(2a) $CH_3 - CH_3 + 3Cl_2 \longrightarrow CH_2 = CCl_2 + 4\ HCl$

(2b) $CH_2 = CH_2 + 2Cl_2 \longrightarrow CH_2 = CCl_2 + 4\ HCl$

(2c) $CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl - CH_2Cl$

Dow has the process flexibility to produce vinylidene chloride by using 1,1,2-trichloroethane as the raw material, or as a co-product of ethane or ethylene chlorination. However, current information indicates that Dow uses 1,1,2-TCE as the raw material, as well as recovering VDC as a co-product of ethylene chloride manufacture. The amount of vinylidene chloride produced from either of these processes depends on the market demands for the various chlorinated products of ethane or ethylene.

3.2 MANUFACTURING SITES

The two companies which are active producers of vinylidene chloride monomer have a total of three plant sites, all located in the south and southwest part of the United States. In all cases, they form an integral part of a petro-chemical complex in which a variety of chlorinated hydrocarbons are co-produced.

The VDC production sites and estimated capacities are shown in Table 3-1.

TABLE 3-1. PRODUCTION SITES AND CAPACITIES FOR VDC, 1976
(PPG Industries, Dow Chemical Co., 1976, 1977)

Company	Plant Site	Estimated Capacity 10^6 lbs/yr.
PPG Industries, Inc.*	Lake Charles, La.	170 to 180
Dow Chemical Co.**	Plaquemine, La. Freeport, Texas	95 to 100

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*By 1978, new process facilities to manufacture, 1,1,1-TCE should reduce the VDC production level to about 75 million lbs.

**A projected capacity expansion is under consideration. Currently the Texas plant has the larger production.

The output of a given chlorinated ethane (or ethylene) derivative from a typical plant complex can be easily changed by adjustment of overall operating conditions. Hence, potential capacity available for the production of VDC monomer is difficult to assess, and fluctuates with market demands. The capacities in Table 3-1 are based on the best available information.

3.3 MANUFACTURING PROCESSES

The chlorination of ethane and ethylene produces a broad spectrum of chlorinated products including ethyl chloride, ethylene dichloride, vinyl chloride, vinylidene chloride, and trichloroethanes. The patent literature describes many processes for the chlorination of these materials under various process conditions that demonstrate the variability of yields of co-produced chlorinated C_2 hydrocarbons.

Typical of these is one described in a British patent (Dow, 1955) issued to Dow Chemical in 1955 in which ethane or mixtures of ethane and ethylene are reacted in a two step process to produce in the first stage vinylidene chloride (32% yield); 1,2-dichloroethane (30% yield) and trichloroethylene (7.1% yield) with a recovery of 8.5% trichloroethane and 15.2% vinyl chloride from the second stage. A modification of this process claimed a yield of vinylidene chloride of 65% (Crauland, 1954).

Because of the diversity of products obtained by the chlorination of ethane and ethylene, the specific process used will vary depending on the technology used by the producers. Both Dow and PPG report that the specific process used to produce vinylidene chloride from one of the products of the more general chlorination processes is the dehydrochlorination of 1,1,2-trichloroethane. The reaction is:

$$CH_2Cl\text{-}CHCl_2 \xrightarrow{(NaOH)} CH_2{=}CCl_2 + NaCl$$

1,1,2-trichloroethane	Vinylidene Chloride	Sodium Chloride

It is believed that, in addition to the direct process shown above, one or both companies obtain a portion of their vinylidene chloride as a "by-product" of the more general chlorination of ethane or ethylene.

Figure 3-1 is a flow diagram of the direct process for producing vinylidene chloride starting with 1,1,2-trichloroethane. Sodium hydroxide solution is mixed with 1,1,2-TCE in a reactor at elevated temperature and pressure. The reactants flow to a dehydration still where the chlorinated hydrocarbons are separated by distillation. The largely aqueous bottoms flow to a stripper where residual vinylidene chloride is removed and flows to the dehydration column. The stripped bottoms, consisting of a solution of sodium chloride in water are recycled to the chlor-alkali plant. The vinylidene chloride from the distillation column is condensed and flows to storage. The bottoms, consisting of high boiling hydrocarbons, are incinerated.

Emissions are controlled by venting all equipment to a common vent header. This is connected to a refrigerated condenser that removes the bulk of the gaseous vinylidene chloride by condensation. The condensate flows back to the dehydration still. VDC-contaminated noncondensables are vented to the atmosphere or incinerated. It is reported that the emission losses are of the order of 0.2 to 0.3 lbs of VDC per 100 lbs of production.

3.4 DEVELOPMENT OF NEW TECHNOLOGY

The chemistry for the production of vinylidene chloride is well established. The process used to produce vinylidene chloride is a function of the market demands for both VDC and various chlorinated hydrocarbons, and the desire to maximize the economic return for the plant complex.

The two companies presently supplying the market have adequate capacity and process flexibility to satisfy the present as well as the probable future demands for VDC. Thus, there is no incentive to change the current technology, as exemplified by the processes described.

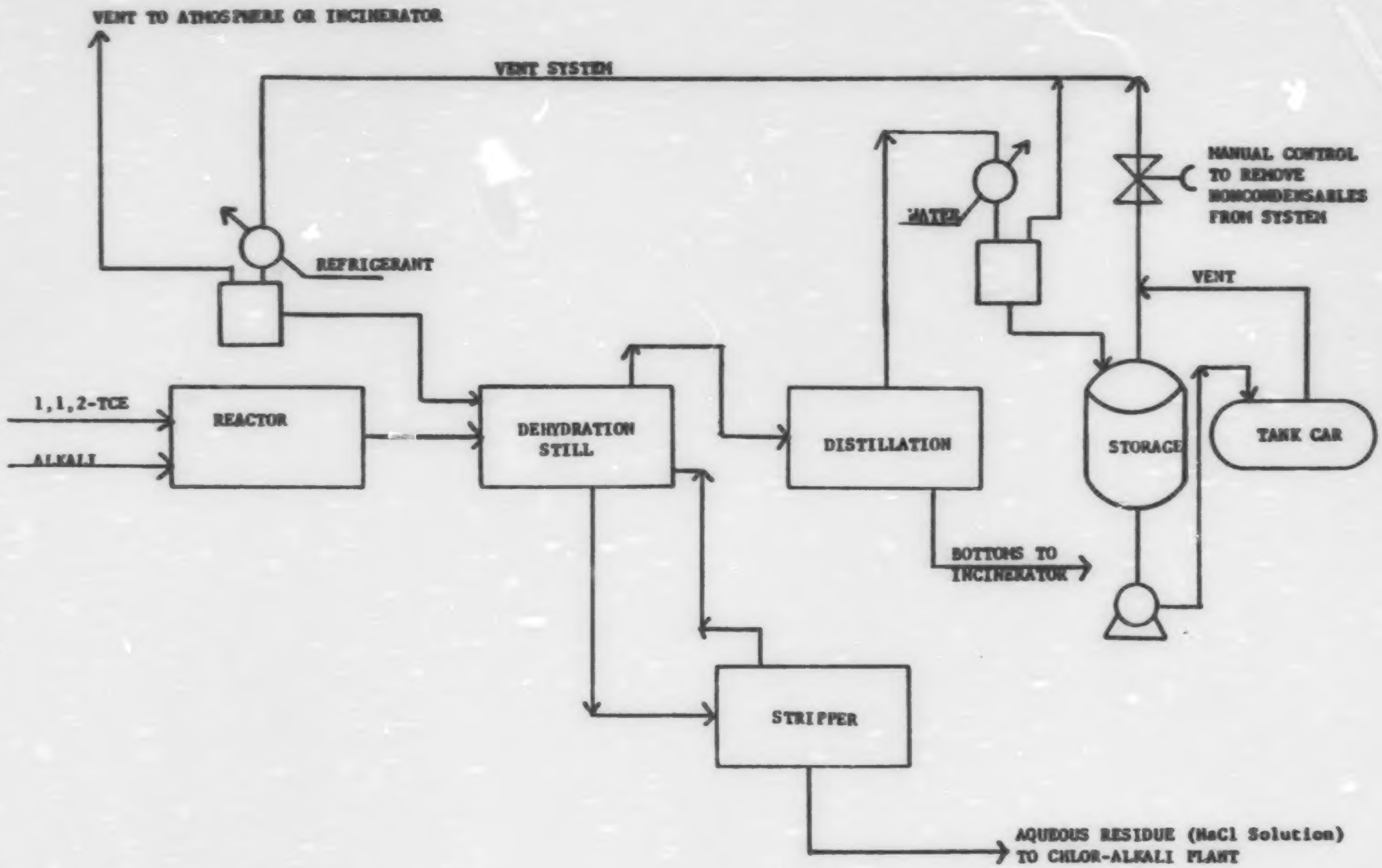

VENT TO ATMOSPHERE OR INCINERATOR
VENT SYSTEM
REFRIGERANT
WATER
MANUAL CONTROL TO REMOVE NONCONDENSABLES FROM SYSTEM
VENT
1,1,2-TCE
ALKALI
REACTOR
DEHYDRATION STILL
DISTILLATION
STORAGE
TANK CAR
BOTTOMS TO INCINERATOR
STRIPPER
AQUEOUS RESIDUE (NaCl Solution) TO CHLOR-ALKALI PLANT

Figure 3-1. VDC Manufacture Via the 1,1,2-Trichloroethane Route

3.5 PRODUCTION MARKETS

Based on the present evaluation of the industry, it is estimated that production of VDC monomer in 1976 will have reached 270 million pounds. About 135 million pounds was polymerized with about 5 million pounds used as a chemical intermediate, and the balance of 130 million pounds consumed captively to produce 1,1,1-TCE.

Demand for VDC for polymerization has grown at an estimated rate of five percent per year for the past five or six years. Its future growth is expected to continue at about the same level, generally following the economy of the country.

From 1963 to 1973, the demand for 1,1,1-trichloroethane grew at an average rate of 9.5 percent per year due to a shift of demand from more polluting solvents. From 1973 through 1976, the overall growth rate dropped to an average of 2.5 percent per year. The reduction in the rate of growth for 1,1,1-TCE is attributed to the slow down in the U.S. economy which decreased the demand for appliances, machines and housing, as well as some saturation of the market for this "non-polluting" solvent. These industries normally consume large quantities of metal products that require solvent degreasing prior to coating.

Since PPG built their plant to produce 1,1,1-TCE, there have been no new installations of plants using VDC. The bulk of VDC produced by PPG is used captively for the synthesis of 1,1,1-TCE. The quantity produced has been a function of PPG's sales of 1,1,1-TCE. Based on industry reports, we project a significant reduction in the VDC produced in the U.S. when PPG puts its new 1,1,1-TCE plant in operation in 1978, using new technology that does not require VDC (see Section 4.2.3).

3.6 TRANSPORTATION AND HANDLING OF VINYLIDENE CHLORIDE

VDC monomer is a volatile liquid that will polymerize in the presence of light, water, air or an oxidizing agent. In the presence of air or O_2 it forms an unstable, explosive peroxide.

Since VDC vapor is heavier than air, it may travel a considerable distance along the ground to a source of ignition and flash back (National Fire Protection Association, 1973). Under certain conditions, it may present a fire or explosion hazard.

VDC is usually stored or shipped with inhibitors such as monomethyl ether of hydroquinone (MEHQ) to prevent polymerization. In the presence of oxygen, peroxide formation and polymerization will occur in uninhibited VDC. Fire presents an additional problem in that toxic hydrogen chloride gas will be evolved. Preventive measures must therefore be taken handling and transporting VDC monomer. These have been established by regulatory and voluntary agencies, and by the vinylidene chloride producers. They are described in the following sections.

3.6.1 Mandatory Regulations for Vinylidene Chloride

Vinylidene chloride is regulated by the Department of Transportation, the Coast Guard and the International Air Transport Association. These regulations are dynamic and regularly modified. A government representative reports that recent revisions of the Hazardous Materials Regulations have resulted in some Coast Guard regulations being incorporated into those of the Department of Transportation (DOT) (Smith, 1976). The International Air Transport Association regulates international air shipments of hazardous materials and those regulations are separate from the DOT. The most current edition of the regulations should be consulted for specific details in any one case.

3.6.1.1 Department of Transportation

The Department of Transportation (DOT) regulates interstate shipment by common carrier, truck, rail, or air. Its rules are published in the Code of Federal Regulations and updated in the Federal Register. They indicate the proper shipping container, shipping documents, and the form and content of labels and placards required. On Janaury 3, 1975, Congress established the Transportation Safety Act of 1974 to improve the regulatory and enforcement authority of the Secretary of Transportation. By this act, it is hoped DOT will be able to assess adequately the risks inherent in the transportation of hazardous materials such as VDC in commerce. The most recent update to DOT shipping regulations was published in the Federal Register on September 27, 1976 (Department of Transportation, 1976).

A summation of the transportation and shipping regulations for vinylidene chloride is shown in Table 3-2. Responsibility for insuring that these standards are met rests with the manufacturer and the shipper.

3.6.1.2 Coast Guard

The Coast Guard classifies vinylidene chloride as a Grade A flammable liquid which must be shipped inhibited. Currently, the Coast Guard uses DOT regulations for VDC container specifications as shown in Table 3-2. Where the container is itself a vessel such as a ship or barge, it is regulated under Title 46 - Shipping, of the Code of Federal Regulations (1975). New regulations for tank barge requirements are in preparation, but a Coast Guard representative (Walker, 1976) states that present barge requirements are as follows:

(1) A double skinned type 2 tank barge is to be used under conditions of ambient temperature and atmospheric pressure.

(2) Independent gravity tanks

(3) Pressure vacuum valves

(4) Type 2 piping class (normal barge requirements)

(5) Class P_2 controls*

---

*Class P_2 controls require:

1) one (1) manually operated stop-off valve
2) one (1) excess flow valve
3) one (1) remote-operated, quick closing, shut-off valve at each cargo base connection when in use
4) no tank penetration shall be less than 1" in diameter

TABLE 3-2. RULES AND REGULATIONS FOR TRANSPORTING VINYLIDENE CHLORIDE

(Department of Transportation, 1976)

Proper Shipping Name: Vinylidene Chloride (inhibited)*

Hazard Class: Flammable Liquid

173.115(a,d): Defines a flammable liquid as any liquid which has a flash point below 100°F (37.8°C). A flash point being the minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.

Labeling Requirements

172.519 (a-g): Regulations concerning the construction of hazard placards.

172.542 (a,b): Specific regulations for "flammable liquid" placard.

Packaging Requirements

173.118 (a)(1): Regulates the shipment of small quantities. The liquid must be packed in metal containers not over 1 quart capacity each, packed in strong outside containers.

173.119(a)(1-25): This section gives packaging regulations for large quantities of VDC. It gives specifications for packages which contain 5 gallons up to specifications for tank cars.

Maximum Net Quantity in One Package

Passenger-carrying aircraft or railcar:	1 quart
Cargo Only Aircraft:	10 gallons
Cargo Vessel:	No quantity specified but must be stored under deck away from heat according to 176.63(d).
Passenger Vessel:	1 quart (is regulated by Section 173.118(a)(1)).

---

*VDC is always shipped inhibited. No specifications for the uninhibited material.

(6) Environmental control: nitrogen padding

(7) Forced venting in cargo handling space

(8) Adequate fire protection

(9) No aluminum, copper or their alloys for pipes, fittings, valves, or materials which come in contact with VDC.

(10) Class I electrical hazard group

Title 46 also contains provisions for the inspection and certification of unmanned tank barges and tank vessels (Code of Federal Regulations, 1975).

3.6.1.3 International Air Transport Association

The International Air Transport Association (IATA) publishes a detailed handbook of regulations for the international air shipment of hazardous materials. Sax (1968) states that under IATA rules uninhibited VDC is not acceptable for either passenger or cargo carriers. Inhibited VDC is classed as a flammable liquid, and given a red label. Passenger aircraft may carry one liter of chemical while cargo aircraft is allowed 40 liters of VDC. A comparison with DOT regulations shows that the IATA allows the same amount of VDC on board cargo aircraft as the Department of Transportation.

3.6.2 Voluntary Regulations for Vinylidene Chloride

3.6.2.1 American Conference of Governmental Industrial Hygienists (ACGIH)

The ACGIH issues recommendations for acceptable levels of chemicals in the work environment. Based on experiments by Prendergast et al. (1967) and Gage (1970), the American Conference of Governmental Industrial Hygienists (1971) has set the threshold limit value for airborne concentrations of vinylidene chloride at 10 ppm. The threshold limit value as defined by the Manufacturing Chemists' Association (1972) "represents conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse affect."

3.6.2.2 National Fire Protection Association (NFPA)

The NFPA's "Committee on Fire Hazards of Materials 704M" (National Fire Protection Association, 1973) has developed a numerical rating system for identification of hazardous materials with respect to fire hazards. The system allows ratings of hazards on a scale of zero (non-hazardous) to four (extremely hazardous) in the categories of health, fire and reactivity. Table 3-3 presents these hazard ratings for VDC.

The NFPA has also developed a classification system of hazardous locations and the appropriate wiring and electrical equipment to be used for that location. Under the National Electrical Code, locations are designated according to classes, divisions and atmospheres. Standards for handling VDC in conjunction with electrical equipment are discussed under the Article 500, Class 1, Division 2 location, which is defined as a location:

> (1) in which volatile flammable liquids or flammable gases are handled, processed, or used, but in which the hazardous liquids, vapors, or gases will normally be confined within closed containers or closed systems from which they can escape only in case of accidental rupture or breakdown of such containers or systems, or in case of abnormal operation of equipment;
>
> (2) in which hazardous concentrations of gases or vapors are normally prevented by positive mechanical ventilation, but which might become hazardous through failure or abnormal operation of the ventilating equipment; or
>
> (3) that is adjacent to a Class I, Division 1 location, and to which hazardous concentrations of gases or vapors might occasionally be communicated unless such communication is prevented by adequate positive-pressure ventilation from a source of clean air, and effective safeguards against ventilation failure are provided.

To determine the relative hazards of flammable chemicals in relation to their volatility, the NFPA also assigns chemicals by atmosphere groups. Atmospheres are determined by a comparison of the chemical to a representative chemical for each group. At the present

TABLE 3-3. NATIONAL FIRE PROTECTION ASSOCIATION HAZARD RATINGS FOR VINYLIDENE CHLORIDE UNDER FIRE CONDITIONS

(National Fire Protection Association, 1975)

HAZARD	RATING	DESCRIPTION
HEALTH HAZARD Type of Possible Injury	2	Materials hazardous to health, but areas may be entered freely with self-contained breathing apparatus. Highly toxic HCl gas is evolved during thermal degradation. (See Section 3.6)
FLAMMABILITY Susceptibility of Materials to Burning	4	Very flammable gases, very volatile flammable liquids, and materials that in the form of dusts or mists readily form explosive mixtures when dispersed in air. Shut off flow of gas or liquid and keep cooling water streams on exposed tanks or containers.
REACTIVITY Susceptibility	2	Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Includes materials which can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. Also includes those materials which may react violently with water or which may form potentially explosive mixtures with water. In advanced or massive fires, fire fighting should be done from a safe distance or from a protected location.

time 300 new chemicals are being added to the Group Atmosphere list, for which the physical testing is being done by the National Academy of Science. The physical parameters used are the flash point, auto-ignition point and the vapor density. VDC is tentatively classified as a Group D Atmosphere, in which gasoline is the representative chemical (Beneditti, 1977).

3.6.2.3 Other Regulatory Agencies

An examination of rules administered by the Interstate Commerce Commission revealed no shipping regulations for vinylidene chloride.

While the Occupational Safety and Health Administration (OSHA) does not directly regulate vinylidene chloride, OSHA currently advises that the threshold limit value of 10 ppm set by the American Conference of Governmental Industrial Hygienists should be followed (Crenshew, 1976).

3.6.3 Handling Procedures and Hazards

Intelligent handling of VDC requires proper ventilation and the elimination of ignition sources. Two of these precautionary measures as outlined by PPG (1975) are as follows:

> Containers should not be left unattended and open, giving off vapors. Nozzles for steaming, hoses and purging-equipment must be properly grounded to reduce the possibility of an arc from an accumulated charge of static electricity.

Special procedures have been developed for workmen handling vinylidene chloride monomer as inhibited liquid VDC can be irritating to the skin and eyes after a few minutes contact. Shelton, et al. (1971) believes this irritation is caused by the volatile VDC evaporating, thereby leaving the inhibitor to accumulate and cause local skin irritations or burns. It is recommended, therefore that protective eye gear and clothing be worn to prevent chemical contact and that once contaminated, clothing be immediately removed. Wearing apparel splashed by VDC should be washed thoroughly before reuse, especially shoes, which should also be aerated. Personnel should bathe thoroughly to remove any monomer that may have penetrated the skin.

As noted earlier in this section, vinylidene chloride is highly volatile and its vapor is heavier than air. PPG (1975) concludes that "since the VDC odor threshold lies between 500 and 1000 ppm, the odor is not an adequate warning to prevent overexposure. Persons working around open containers of VDC should stand upwind of vapors or get the cross wind." Because overexposure to vapor for even a few minutes can lead to anesthesia and unconsciousness, proper respiratory equipment is required especially when concentrations of VDC cannot be kept under the 10 ppm threshold limit value (see Section 3.6.2). Shelton, et al. (1971) states that the high volatility of vinylidene chloride will readily produce excessive vapor concentrations from a spill or leak. In such situations and where an oxygen deficiency might exist, an air-supplied mask or self-contained breathing apparatus should be used. Persons responsible for cleaning up the spill or diking the leak should wear spark-proof shoes and use spark-proof tools.

Medical attention is required for all cases of overexposure and for persons contaminated by or accidentally swallowing VDC.

In addition to clothing protection for workmen, transporting and unloading VDC cargo requires precautionary techniques. Specific instructions are provided by the manufacturer. In general it is most important to prevent ignition. Static discharge is accomplished by grounding arrangements. All wiring and electrical equipment should be explosion-proof and in accordance with the National Electric Code (National Fire Protection Association, 1975). Additional instructions for the general handling of flammable liquids, such as VDC and for sampling VDC in tank cars and tank truck shipments are supplied by the Manufacturing Chemists' Association, Inc. (1963, 1975).

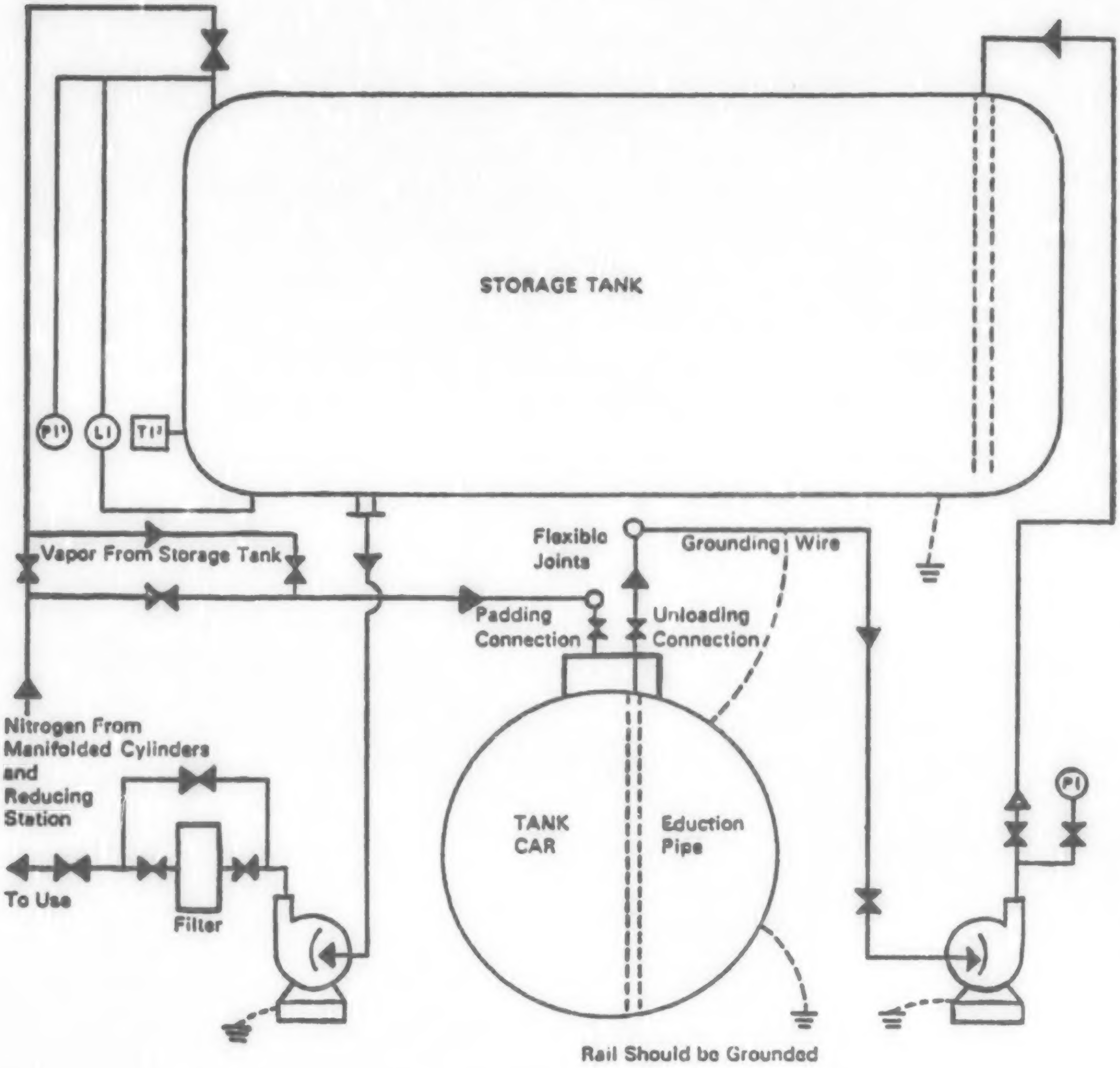
3.6.4 Transportation Methods

Vinylidene chloride can be shipped in drums, tank wagons, rail tank cars, or barge. Regardless of vessel, it is shipped under a nitrogen blanket at atmospheric pressure. PPG Industries (1975) states that "nitrogen used in vinylidene chloride service should have a maximum oxygen content of 100 ppm." In all cases, the tank wagons or rail tank cars are used solely for the transportation of VDC. A typical tank car capacity as described by PPG contains 11,000 gallons or 111,000 pounds of material. Unloading of the tank trucks or cars is done following instructions supplied by the manufacturer; Figure 3-2 shows a typical tank car unloading station for vinylidene chloride. When emptied, the tank cars are normally returned directly to the monomer manufacturer. Because they are in "dedicated service" the tank wagons/tank cars are not washed nor vented to the atmosphere.

Drum containers are available in 5 to 55 gallon sizes and are non-returnable. A sample drum size is DOT specification 17C, which has a net weight capacity of 500 pounds. In Section 173.119, part (a) (4) of 41 Fed. Reg. 42474, Specification 17C states that "metal drums (single-trip), with openings not exceeding 2.3 inches in diameter" are to be used. When emptied, the drums are flushed with water to prevent explosive peroxide formation and are then filled with water to displace all air. The inside of the drum is washed with a 5% by volume solution of methanol in perchloroethylene at room temperature to disolve any peroxide compound that may have formed.

3.6.5 Storage Methods

The National Fire Protection Association (1973) recommends that outside or detached storage of VDC containers be used and that


STORAGE TANK
PI¹
LI
TI²
Vapor From Storage Tank
Flexible Joints
Grounding Wire
Padding Connection
Unloading Connection
Nitrogen From Manifolded Cylinders and Reducing Station
To Use
Filter
TANK CAR
Eduction Pipe
PI
Rail Should be Grounded

[1] RANGE: Full vacuum to 100 psig.

[2] RANGE: -20°F to 200°F

Figure 3-2. Typical Tank Car Unloading Station for Vinylidene Chloride
[Reprinted from Vinylidene Chloride: Handling/Properties/ Reactivity Ratios by PPG Industries by permission of PPG Industries. (Year of first publication, 1975.)]

storage containers be protected from physical damage. Inside storage is provided for by a standard flammable liquids storage room or cabinet. Oxidizing materials must be kept away from VDC. It is important that storage areas be selected to comply with local codes or authorities.

In all cases where the monomer is pumped from tank truck or tank car to plant storage or from storage to process vessel, a closed vent loop system should be used. There should thus be no venting loss of vinylidene chloride to the atmosphere from VDC transfer operations.

3.6.5.1 Construction Materials

The chemical reactions between VDC and other substances must be accounted for in selecting construction materials for storage containers. The following have been recommended (PPG, 1975): Steel, stainless steel and nickel should be used as materials for storage tanks, pumps, valves, fittings and pipe which handle vinylidene chloride. For uninhibited VDC, nickel is the material of choice. Cast iron is not acceptable because iron can cause vinylidene chloride to polymerize. Since many lubricants are attacked by VDC, valves and fittings should be of a type that does not require lubrication. As it is possible for VDC to form explosive compounds with copper, aluminum and their alloys, these metals must not be used in storage and handling equipment (Dow, 1975).

3.6.5.2 Drums

Drums should be stored unopened in a cool, dry place for not more than four months. Since bulging of a drum may indicate VDC monomer decomposition with the possible formation of an explosive peroxide compound, disposal precautions and procedures as described in Section 3.6.6.2 should be taken. Recommended safe practices can also be found in the Manufacturing Chemists' Association (1960) safety guide for flammable liquids.

3.6.5.3 Tanks

VDC must be protected from contact with oxygen, sunlight, water and other polymerization initiators. In the absence of these substances, and when dry and blanketed by nitrogen with a maximum of 100 ppm oxygen, inhibited VDC can be stored indefinitely (PPG, 1975). Tanks for VDC should be designed for working pressure of 30 psig and be equipped with a pressure-relief valve, level guage, pressure guage, and remote shutoff valves. Usually these tanks are 10,000 to 20,000 gallons in size, are above ground, and in some instances, they are cooled by the use of brine coils. A water spray system keeps the tanks cool in case of fire. Adequate dikes and drainage are provided to confine and dispose of the liquid in case of a tank rupture.

3.6.6 Accident Procedures

3.6.6.1 Fires and Explosion

In advanced fires, fire fighting is done from a safe distance or from a protected location. Dry chemical, foam or carbon dioxide agents are materials that can be used as extinguishers. The National Fire Protection Association (1973) concludes:

> "Water may be ineffective, but should be used to keep fire-exposed containers cool.... If it is necessary to stop a leak, use water spray to protect men attempting to do so."

PPG (1975) states however that "if the source of the vinylidene chloride monomer leak has not been closed off, do not attempt to extinguish a large fire because hot metal can re-ignite an unburned vapor cloud."

The explosive nature and handling procedures of the peroxide compound formed by the reaction of VDC and air is discussed in

Section 3.6.2. Extreme caution should be exerted in separating precipitated polymer and its adsorbed peroxide.

3.6.6.2 Spills and Leaks

Spills and leaks from vinylidene chloride containers and equipment should be handled promptly. All possible sources of ignition must be eliminated and only properly protected and trained personnel should be allowed to remain in the vicinity of the spill or leak.

The following clean-up procedures are recommended (PPG, 1975; Dow, 1975):

(1) Keep people away and do not permit smoking.

(2) If it can be done without personal risk, shut off a leak.

(3) Dike the liquid from a large spill and pump it into a salvage tank.

(4) Spilled vinylidene chloride should not be deliberately ignited.

(5) Water spray can be used to "knock down" vapors.

(6) If a spill is small, cover it with an absorbent material such as sand. After the liquid has been absorbed, remove the sand to a safe area. Immediately flush the sand with a lot of water, but don't let the water run off into a sewer.

3.7 ENVIRONMENTAL MANAGEMENT FOR VINYLIDENE CHLORIDE MONOMER PRODUCTION

According to information supplied by the manufacturers of vinylidene chloride monomer, overall losses of VDC from all sources is of the order of 0.003 pounds per pound manufactured. Estimated losses of VDC monomer at the three manufacturing sites are shown in Table 3-4 and Figure 3-3.

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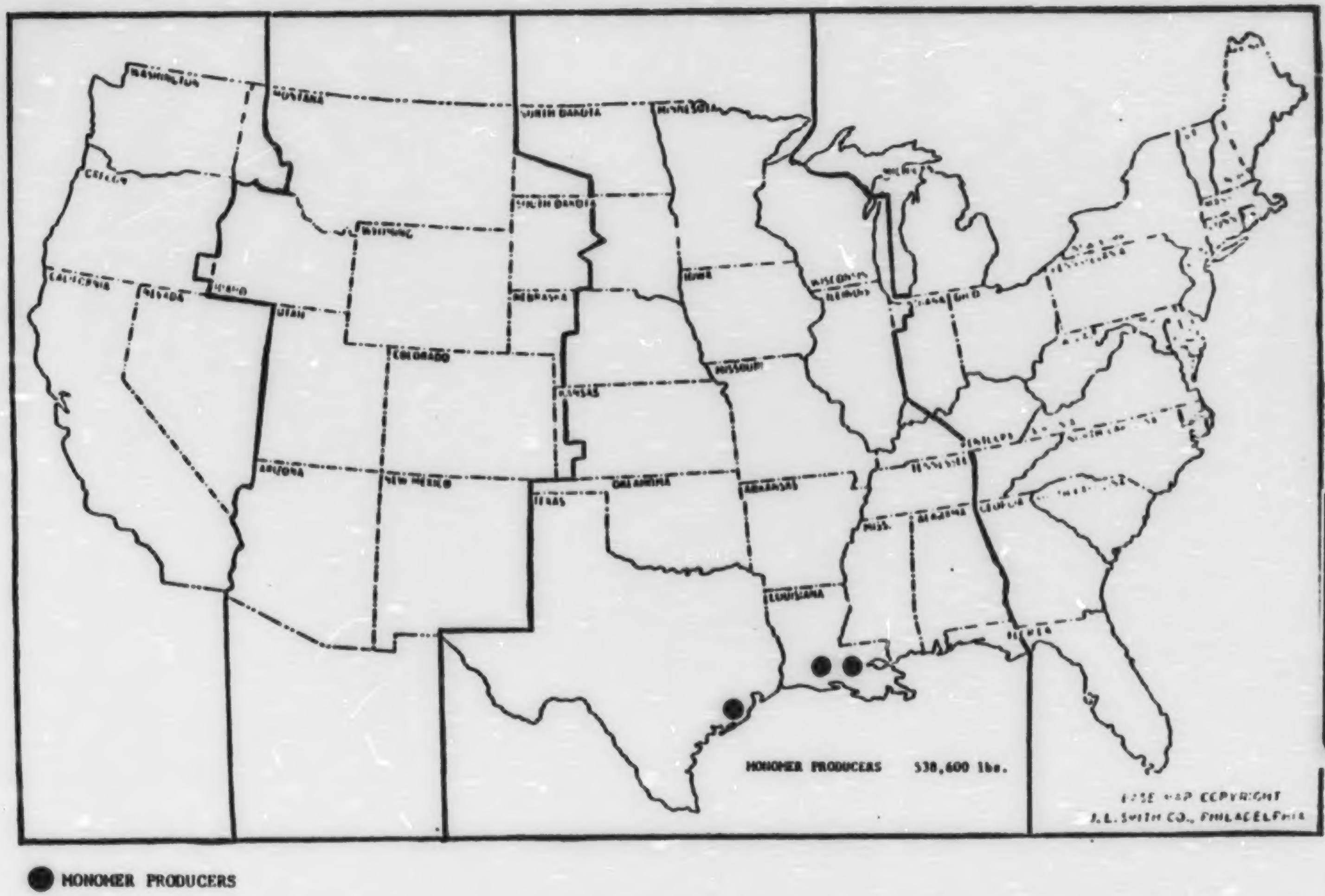
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISS.
ALABAMA
GEORGIA
FLORIDA
PENNSYLVANIA
MONOMER PRODUCERS 538,600 lbs.
BASE MAP COPYRIGHT
J.L. SMITH CO., PHILADELPHIA
● MONOMER PRODUCERS

Figure 3-3. Estimated Losses for VDC Monomer from Monomer Producers in 1975
(Industry Sources, 1976)

TABLE 3-4. ESTIMATED LOSSES OF VDC BY MANUFACTURING SITE
(Industry Estimates)

Company		Losses lbs/yr.** 1975	Losses lbs/yr.** 1976
Dow Chemical Co.	Freeport, Tex.	100,600	*
	Plaquemine, La.	238,000	*
PPG Industries	Lake Charles, La.	200,000 to 300,000	200,000 to 300,000
	Total	538,600 to 638,000	

*Somewhat higher due to increased production in 1976.
**Estimates by manufacturer.

PPG Industries Inc. reported that a substantial reduction in emissions compared to the 1974 data as reported by Milgrom (1976) were effected by installing a new vent control system in which all major sections of the process, including storage tanks were tied together into a common header. The vented gases then pass through a refrigerated condensing unit that removes about 90% of the VDC monomer that had been previously lost.

Dow's air pollution control system is reported to utilize a similar process in which all equipment and storage tank vents are connected to a common header. The vent gases then pass through condensing equipment prior to venting to the atmosphere.

Data supplied by Dr. J. Pennington of the Texas Air Control Commission (1976), confirmed the emission losses submitted by Dow Chemical Co. for the Freeport plan . About 75% of Freeport plant emissions were from process, the balance from storage and filling operations,according to the Texas Air Control Commission data.

Both monomer producers indicated that liquid losses were nil. Any waste bottom streams from distillation processes were destroyed by incineration. If any leaks should occur (for example, pump seals) VDC would vaporize almost immediately. Since the process for the manufacture of chlorinated hydrocarbons is continuous, equipment clean-out operations familiar to batch processes is not required. There are, therefore, no wash waters to be treated before disposal.

Tank cars and tank trucks used for shipping VDC monomer are in "dedicated service" and do not have to be cleaned prior to filling and shipping.

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SECTION IV. CONSUMPTION PROCESSES STUDY

4.1 PRESENT STATUS OF THE INDUSTRY

Vinylidene chloride currently has three commercial uses:

a) the manufacture of 1,1,1-trichloroethane (methyl chloroform)

b) the production of a wide variety of copolymers

c) the synthesis of other chemical intermediates such as the alkoxy chlorinated hydrocarbons

1,1,1-trichloroethane and chlorinated chemical intermediates are manufactured by PPG and Dow respectively using captive VDC monomer. The use of vinylidene chloride in the manufacture of these chemicals is determined largely by the economics of competing processes.

VDC monomer is sold by PPG and Dow Chemical as a merchant chemical to companies who manufacture a variety of polymeric materials. In addition, Dow Chemical is a major VDC consumer for captive polymerization to produce various products. The homopolymer of VDC is a crystalline, brittle material that has substantially little commercial value. When VDC is copolymerized with other monomers, a number of useful compounds are produced. The major comonomers used in the polymerization of VDC are vinyl chloride, acrylic acid, methacrylic acid, acrylonitrile, butadiene, and styrene.

Currently about 120 million pounds of VDC are polymerized by 13 companies. Of these, Dow Chemical Co., one of the two producers of the monomer, produces more than 50% of the VDC copolymers made in the United States.

VDC copolymers find applications in the following industries:

Flexible Packaging Materials

- as a barrier coating on other flexible packaging materials
- as a coextruded or multilayer film
- as a monolayer film

Textiles

- as a flame retardant modacrylic fiber when polymerized with acrylonitrile.
- as a flame retardant carpet backing when polymerized with butadiene and styrene

Other

- as a plastic pipe
- as a coating for steel pipe
- as an adhesive

The barrier coating market for VDC polymers has reached the stage of mature growth. Future growth of this market will tend to parallel that of the food packaging industry. The biggest shift will occur in the type of substrate film to be coated, as for example, the shift from cellophane to polypropylene.

VDC competes on the basis of cost vs. performance with other materials that can provide improved flame retardant characteristics, such as alumina and organic phosphates. Performance is dictated by both governmental and industrial regulatory agencies. As these become more stringent for plastics and textiles, the greater will be the market opportunity for more expensive materials such as VDC.

In the following section, the major uses of VDC will be discussed from the viewpoint of:

- Current processes used to produce the major end product from VDC.
- Alternate processes for producing these end products.
- The market structure and consumption patterns for the end products

Estimated consumption patterns of VDC in 1976 are shown in Table 4-1.

4.2 1,1,1-TRICHLOROETHANE MANUFACTURE

1,1,1-Trichloroethane, commonly known as methyl chloroform, is manufactured commercially using several different process routes:

- Hydrochlorination of vinylidene chloride
- Chlorination of vinyl chloride
- As a coproduct of the direct chlorination of ethane and ethylene

At present, PPG is the only manufacturer of 1,1,1-trichloroethane using vinylidene chloride as the starting material.

4.2.1 Manufacture from Vinylidene Chloride

1,1,1-Trichloroethane is manufactured from VDC in PPG's chlorinated hydrocarbon complex in Lake Charles, La., using a continuous hydrochlorination process shown in the flow diagram, Figure 4-1.

The equation for this reaction is:

$$CH_2 = CHCl_2 + HCl \longrightarrow CH_3 - CCl_3$$

Vinylidene chloride is fed together with hydrogen chloride into a reactor operating at an elevated temperature. The gases leaving the reactor are fractionated. Unreacted HCl and VDC are recovered from the fractionating column and recycled to the hydrochlorination reactor. The crude 1,1,1-TCE product from the bottom of the fractionator is purified by distillation in a second column. The distilled 1,1,1-TCE product, containing a maximum of 100 ppm VDC, goes to a blend tank for addition of corrosion inhibitor, and then to storage.

TABLE 4-1. ESTIMATED CONSUMPTION PATTERNS FOR VINYLIDENE CHLORIDE, 1976, MILLIONS OF POUNDS

(Industry and M. Sittenfield and Associates Estimates)

Manufacture 1,1,1-Trichloroethane		130
Polymerization		126
PVDC Resin		
Barrier Coatings	26.8	
Cellophane Coating	16.2	
Film and Molded Products	46.2	
Export	20.0	
Flame Resistant Resins with VDC content		
Modacrylic Fiber	9.0	
Carpet Backing	7.5	
VDC Losses		
VDC Manufacture - Vented		.55
VDC Polymerization		
Vented to Atmosphere		.56
Equivalent VDCM content of solid PVDC in sewered wastes		7.4
Other Uses (Chemical Intermediate)		5.0
TOTAL ESTIMATED VDC MANUFACTURED IN U.S.		270

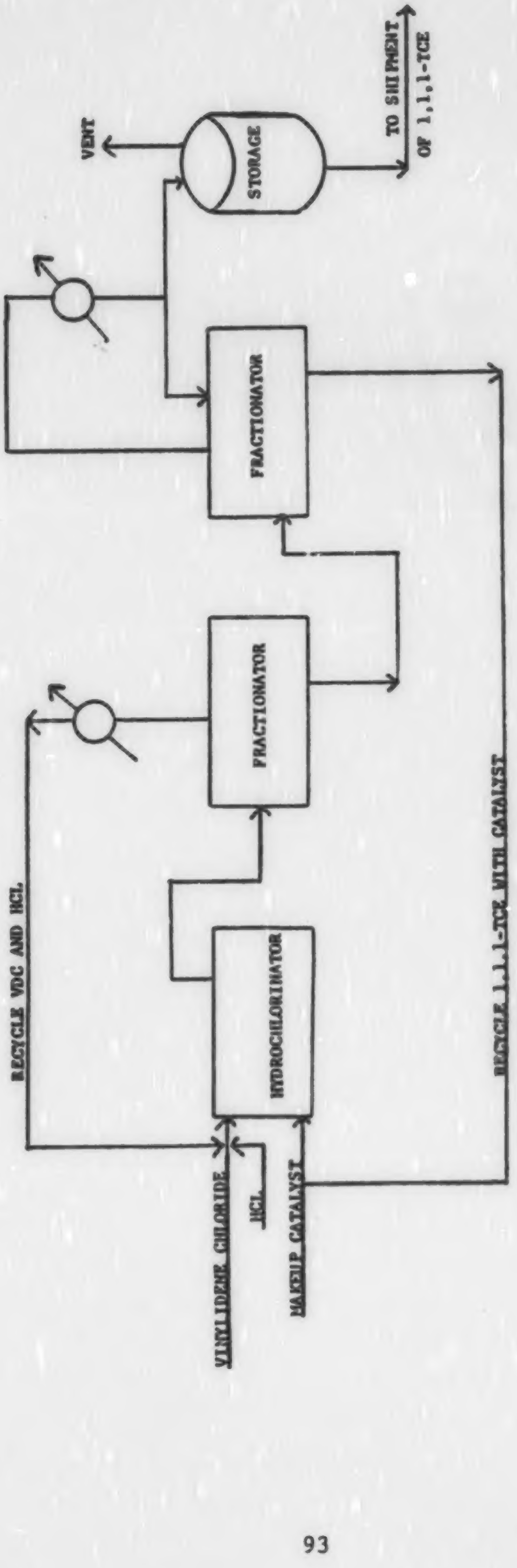

VINYLIDENE CHLORIDE
HCL
MAKEUP CATALYST
HYDROCHLORINATOR
RECYCLE VDC AND HCL
FRACTIONATOR
FRACTIONATOR
RECYCLE 1,1,1-TCE WITH CATALYST
STORAGE
VENT
TO SHIPMENT OF 1,1,1-TCE

Figure 4-1. Block Flow Diagram for 1,1,1-Trichloroethane Production

The process is totally enclosed and operates with no vents to the atmosphere and the possibility of VDC process emissions or other process losses is almost nil.

The only possibility of VDC emission would result from the vents on the inhibitor blend tanks and product storage tanks, due to the small amount of VDC monomer (100 ppm) residual in the final distilled product. This, under worst conditions, would not exceed 17,500 lbs. per year. However, it is improbable that all of this loss would occur at the manufacturing site. Further emissions from these sources are controlled by piping the tank vents to a common system connected to an incinerator.

4.2.2 Alternate Routes of Manufacture

As stated above , other processes for the manufacture of 1,1,1-TCE are used. The specific process used by any of the several 1,1,1-TCE producers is dependent on the company's technology, their product mix, and the economics of the overall operation.

In the first two processes previously listed, 1,1,1-TCE is produced from vinyl chloride or vinylidene chloride which would have been synthesized from ethylene dichloride.

The third process is a more complex process since the direct, continuous non-catalytic chlorination of ethane produces a variety of chlorinated hydrocarbons including ethyl chloride, vinyl chloride, vinylidene chloride and 1,1-dichloroethane. The economics of producing 1,1,1-TCE from this process is dependent on the recycling of ethyl chloride, 1,1-dichloroethane and other chlorinated products.

According to Lowenheim and Moran (1975), over 60% of 1,1,1-trichloroethane is produced from vinyl chloride, 30% from vinylidene chloride and the balance from ethane.

It is believed that since Ethyl Corporation stopped production of 1,1,1-TCE in 1976, the amount produced from ethane has diminished.

4.2.3 Development of New Technologies

It is reported that PPG, the only company presently using VDC as the raw material for 1,1,1-TCE, will not use VDC as the raw material for its new plant scheduled for operation in 1978. The new plant, with an announced capacity of over 300 million pounds of 1,1,1-TCE yearly, will more than double present capacity (Chemical Marketing Reporter, 1977) Details of the process technology have not been made public. This change in process will release more of PPG's existing VDC capacity for merchant sale, should the demand picture require additional production.

4.2.4 Environmental Management of VDC in 1,1,1-Trichloroethane Processes

Emission losses of VDC from the PPG plant during the production of 1,1,1-TCE have been reported to be non-existent. The reason given is that the process is a continuous operation. Separation of unreacted VDC monomer occurs in a distillation column from which it is recycled directly to the hydrochlorination reactor.

Handling of the feed VDC is done in a completely closed system with venting of the feed tanks back to the storage tanks.

The product blend and storage tanks are vented to a common system that goes to an incinerator. Hence the potential loss of VDC from these sources would be negligible.

VDC-produced 1,1,1-TCE is reported to contain up to 100 ppm of VDC monomer. Based on a probable production of 1,1,1-TCE from VDC of 175 million pounds per year, the possible distribution of VDC from this source could equal 17,500 lbs. per year. However, in terms of commercial or environmental contact, distribution of 1,1,1-TCE is so widespread that local concentrations would not exceed an order of magnitude of 0.004 lbs. per square mile, per year.

4.3 POLYMERIZATION PROCESSES

Vinylidene chloride copolymers are manufactured in the form of latex emulsions, powder resins, or modacrylic fibers. Three basic processes are used:

- Emulsion polymerization
- Suspension polymerization
- Solution (solvent) polymerization

The selection of one technique over another is determined chiefly by the end use. For example, emulsion processes are used historically to produce coating latexes. Both suspension and emulsion techniques are used to produce solid polyvinylidene chloride (PVDC) resins used for solution coating, molding or extrusion. Solution polymerization may be used for manufacture of modacrylic fiber. Each of these techniques is used to produce polymers of differing physical properties, which can be utilized more readily in subsequent converting operations. The majority of PVDC is manufactured using emulsion polymerization techniques.

The characteristics of the polymer are strongly influenced by the content of vinylidene chloride. Resins containing more than 50% (typically 70 to 95%) vinylidene chloride exhibit excellent barrier resistance and chemical resistance. Polymers with less than 50% vinylidene chloride, typically 10 to 40%, are used when it is desired to improve the fire retardant characteristics of the base monomer material.

4.3.1 Emulsion Latex and Suspension Polymerization

Emulsion and suspension polymerization processes use essentially the same type of equipment, and are similar in their overall characteristics. They differ in the formulation of the batch, operating conditions of temperature, time and agitation, degree of conversion of the monomer, and techniques for removal (stripping) of residual monomer. Some industry sources indicate that the suspension process is easier to control and that there are fewer "lost" batches that must be sewered.

Vinylidene chloride latexes generally contain 50 to 63% solids, whether produced by emulsion or suspension process. A typical latex polymerization process is shown in Figure 4-2. The vinylidene chloride is fed together with the comonomer, emulsifier, catalyst, water or solvent, stabilizer, and suspension agent into a reactor that has been purged with an inert gas and evacuated. Evacuation removes oxygen from the vessel and assists in the transfer of the raw materials so that venting of VDC to the atmosphere is minimized at this stage of the process.

Heat and agitation are applied for a number of hours (8 to 24) until 90 to 95% conversion has been reached. The reactor contents are then stripped in situ or pumped to a stripper where unreacted VDC and other monomers are removed.

In some plants, unreacted VDC and comonomers are stripped and vented through a vacuum jet system to the atmosphere. In other plants they are condensed, the monomer recovered and recycled.

Solution polymerization is used in connection with production of fiber by means of a spinneret.

4.3.2 Solid Resins

Solid polyvinylidene chloride resins are used in the following applications:

- Extrusion into film
- Coextrusion with other plastic film to form a multilayer film
- Extrusion to produce pipe
- Coating cellophane by dissolving PVDC resin in an organic solvent, forming a lacquer.
- Molding

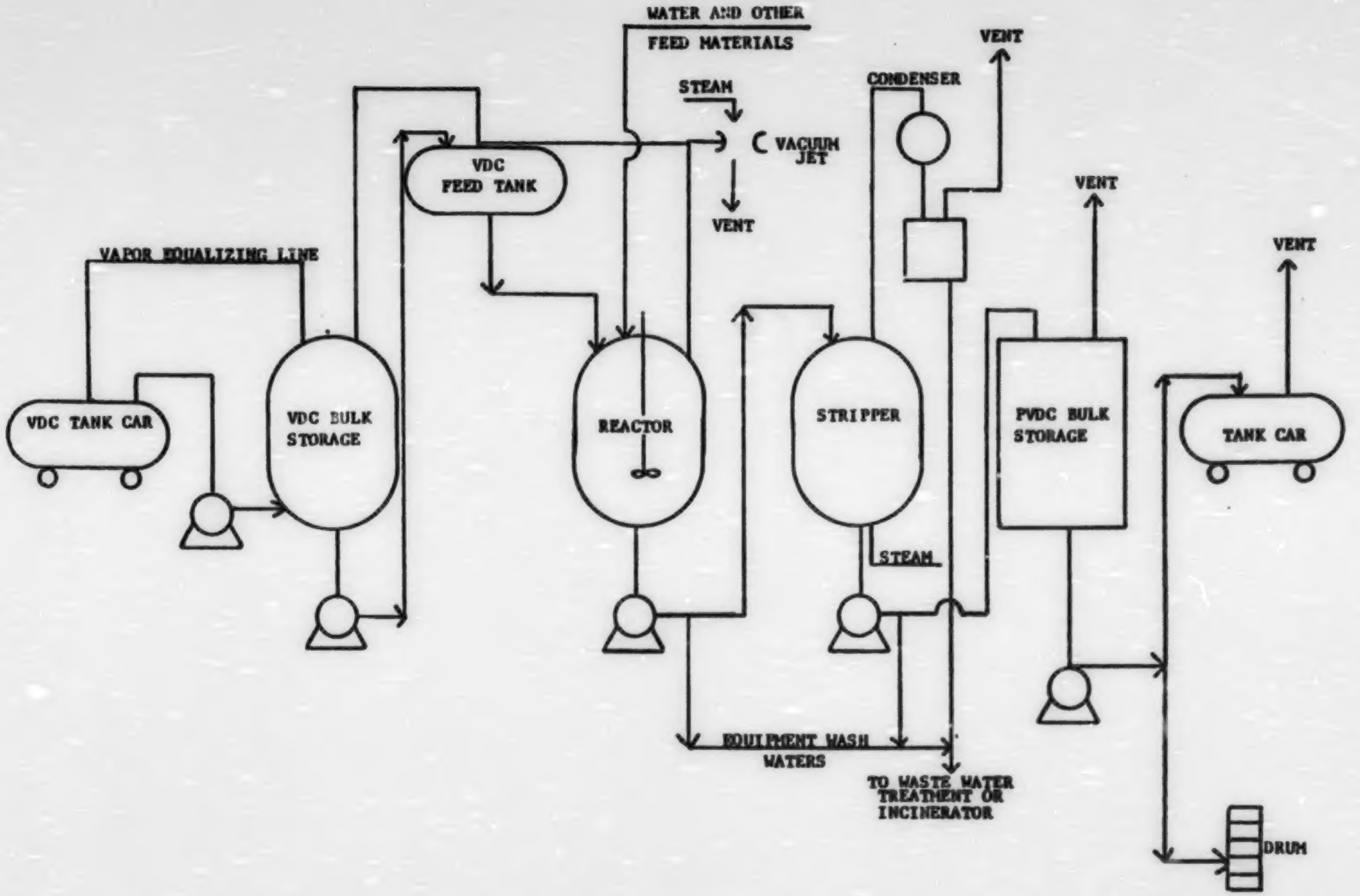

WATER AND OTHER
FEED MATERIALS
STEAM
VACUUM JET
VENT
CONDENSER
VENT
VENT
VENT
VDC FEED TANK
VAPOR EQUALIZING LINE
VDC TANK CAR
VDC BULK STORAGE
REACTOR
STRIPPER
PVDC BULK STORAGE
TANK CAR
STEAM
EQUIPMENT WASH WATERS
TO WASTE WATER TREATMENT OR INCINERATOR
DRUM

Figure 4-2. VDC Latex Polymerization Process

Both suspension and emulsion processes are used as the first step in the production of PVDC resins. Figure 4-3 illustrates a typical process for converting a latex to the powdered resin. In this step of the process, the stripped latex is filtered or centrifuged. The solid resin mass is then dried and packaged in fiber drums or large Gaylord containers. The resin may be used for solution coating of cellophane or other water sensitive films; for extrusion into films, pipe coatings or monofilament fibers; or to produce molded products. Dow Chemical Co. is the sole producer of merchant PVDC resins. DuPont's Circleville, Ohio plant makes some resins for captive use.

4.3.3 Modacrylics

The process for the manufacture of modacrylic fibers parallels that for producing dry resins using emulsion and solution polymerization techniques. The reactant monomer mix for modacrylic fibers contains between 10 and 20% VDC, the balance being acrylic monomers. In this copolymer, the vinylidene chloride is used for its flame retardant properties.

Following polymerization, the latex is dried. Stripping steam and monomer are condensed to prevent emission to the atmosphere, the monomer is recovered for recycling. The waste waters are processed in a conventional waste treatment plant. The dried polymer is dissolved in a suitable solvent and sent to conventional wet spinning processes for fiber formation.

The major producers of modacrylic fibers are listed in Table 4-2.

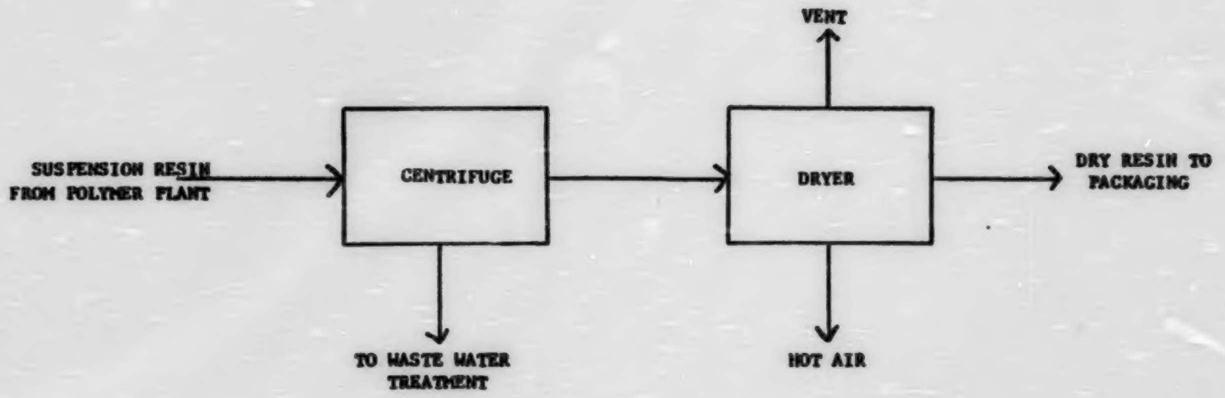

SUSPENSION RESIN
FROM POLYMER PLANT
CENTRIFUGE
TO WASTE WATER
TREATMENT
DRYER
VENT
HOT AIR
DRY RESIN TO
PACKAGING

Figure 4-3. Conversion of Latex to Powdered Resin Process

TABLE 4-2. PLANT SITES FOR POLYMERIZATION OF VINYLIDENE CHLORIDE

COMPANY	SITE	POLYMER TYPE
Dow Chemical Co.	Midland, Mich.	Emulsion Latexes Suspension Resins
	Dalton, Geo.	Specialty Latex
W.R. Grace Chem. Co.	Owensboro, Ky.	Emulsion Latex Specialty Latex
Morton Chemical Co.	Ringwood, Ill.	Emulsion Latex
A.E. Staley Mfg. Co.	Lemont, Ill.	Emulsion Latex
E.I. DuPont	Circleville, Oh.	Emulsion Latex
Rohm & Haas Co.	Knoxville, Tenn.	Emulsion Latex
GAF Corp.	Chattonooga, Tenn.	Specialty Latex
Reichhold Chemical	Cheswold, Del.	Specialty Latex
National Starch & Chemical	Meridosia, Ill.	Emulsion Latex
Tennessee Eastman	Kingsport, Tenn.	Modacrylic Fiber
Monsanto Chem. Co.	Decatur, Ala.	Modacrylic Fiber
American Cyanamid	Pensacola, Fla.	Modacrylic Fiber

4.3.4 Development of New Technologies

The trend in polymerization technology is in the direction of increasing the amount of conversion of VDC into polymer without changing the desirable properties of the end product. Increasing conversion helps to reduce the amount of VDC monomer that is left in the polymer to be removed during the stripping operation. New stripping techniques are also being developed to permit greater recovery of the monomer in a state capable of recycling.

4.3.5 Polymerization Processing by Site

Plant sites using monomer vinylidene chloride for polymerization are shown in Table 4-2.

4.3.6 Environmental Management of VDC Monomer in Polymerization Processes

Polymerization processes can introduce contamination to the environment through emissions of monomer VDC as a gas, and in liquid and solid wastes.

The majority of VDC monomer losses to the environment related directly to the polymerization process are from two main sources:

- Vent losses resulting from transfer of monomer from one vessel to another
- Losses resulting from stripping unpolymerized monomer from the product at the end of the reaction

Other losses to the environment result from periodic washing of the reactors, stripping vessels, and product storage tanks, and disposal of solid wastes resulting from a bad polymerization.

Management of air emission losses due to handling and transfer of VDC monomer from rail car or tank wagon to storage and from storage to reactor is achieved by interconnection of vents between vessels.

Further management during the VDC feed step to the reactor is accomplished by first purging the empty vessel with an inert gas followed by complete evacuation of the vessel. The VDC is then sucked into the evacuated reactor.

Air emission losses resulting from stripping of unpolymerized monomer from the batch is by far the major source of VDC emission. It is estimated that this step accounts for over 95% of VDC monomer losses due to VDC polymerization operations.

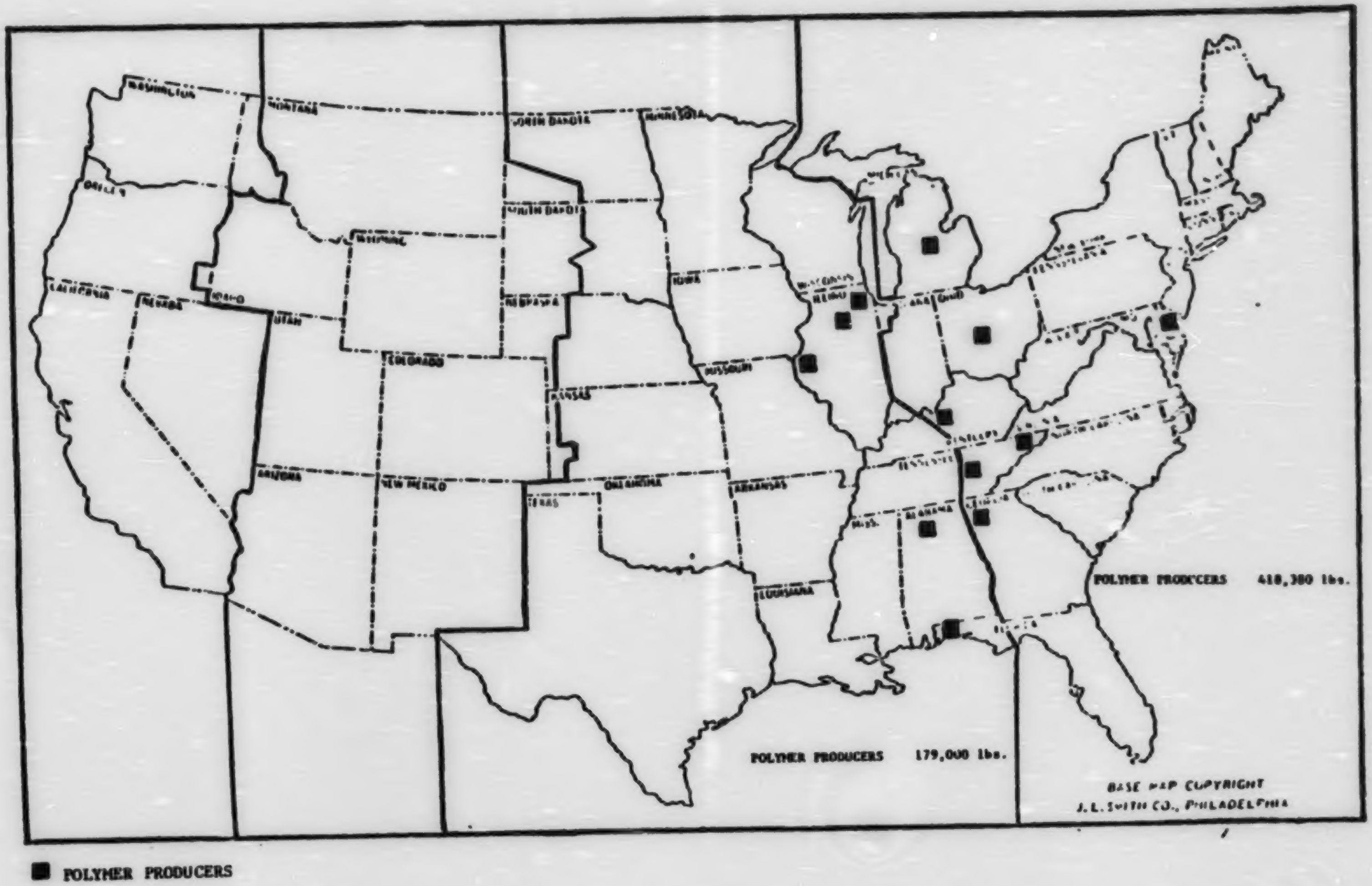
No process currently used in the United States achieves 100% conversion of monomer to polymer. This is due partly to the inability to achieve 100% conversion in a reasonable period of time, and partly because the desired characteristics of the polymer may be altered by prolonging the reaction time. Common practice is to polymerize 90 to 98% of the monomer and to strip substantially all of the residual monomer from the latex product. In smaller capacity plants, this stripped monomer is vented to the atmosphere (see Figure 4-3).

At this point a distinction should be made between rates of polymerization for different monomers polymerized together to form a polymer. Thus, although the average degree of polymerization might be 95%, it should not be assumed that 95% of each of the comonomers has polymerized. It is conceivable that one of the minor component monomers could have achieved a 99% conversion. Because of this it is not possible to equate average degree of polymerization with the quantity of unreacted monomer for a specific chemical.

Typical VDC emission losses as reported by major polymerizing sites are given in Table 4-3. Estimated losses from all polymer producers are displayed geographically in Figure 4-4.

TABLE 4-3. VDC EMISSIONS LOSSES AT MAJOR POLYMERIZATION SITES (Industry Sources, 1976)

Site	Reported emissions lbs VDC/100 lbs. VDC processed	Estimated Emission lbs/yr
A	> 0.3	260,000
B	1.3	90,000
C	2.8	9,000
D	1.0	10,000
E	.64	60,000



WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
OREGON
SOUTH DAKOTA
WYOMING
IOWA
WISCONSIN
CALIFORNIA
NEVADA
IDAHO
NEBRASKA
UTAH
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
COLORADO
KANSAS
MISSOURI
ARIZONA
NEW MEXICO
OKLAHOMA
ARKANSAS
TENNESSEE
TEXAS
MISS.
ALABAMA
LOUISIANA
POLYMER PRODUCERS 418,380 lbs.
POLYMER PRODUCERS 179,000 lbs.
BASE MAP COPYRIGHT
J. L. SMITH CO., PHILADELPHIA
■ POLYMER PRODUCERS

Figure 4-4. Estimated Losses for VDC Monomer from Polymer Producers in 1975 (Industry Sources, 1976)

As can be seen from Table 4-3, emission losses vary from a reported low of 0.3 pounds per 100 pounds of VDC polymerized to 2.8 pounds per 100 pounds. The wide variation is related to the type of product manufactured and to the volume of VDC polymerized.

The smallest emission loss was reported by a company that polymerizes a large quantity of VDC where the quantity of VDC emitted is sufficient to justify control equipment.

The largest emission loss was reported by a company that polymerized less than 500,000 pounds of VDC per year. This company noted that the amount of emission loss was so small that the cost of installing control equipment would make the operation uneconomical.

VDC latexes fall into two classes:

(1) Latexes, used principally in the production of films, or in coatings for paper and plastic, that contain over 50% VDC (typically 85 to 90%)

(2) Specialty latexes in which the percent VDC is below 50% used in the production of fire retardant rug backing

In the case of specialty latexes, the conversion is typically in the 90% range. For this group of products, it is estimated that VDC consumption is on the order of 7 to 8 million pounds per year.

Although average conversion is about 90%, it is reported that smaller VDC concentrations tend to react more completely. The composition of the vent gases is such that conventional emission control systems using either condensation or incineration would be too costly to install and would substantially increase energy demands and costs.

For the bulk of the copolymers, containing over 50% VDC and used for films and coatings, the degree of monomer conversion is between 90 and 98%. For the large volume VDC polymer manufacturers, technology improvements and control systems have been feasible.

One company that produces approximately 75% of all VDC polymer products, reported 1975 emissions of 0.27% equal to 258,000 lbs. per year.

If the efficiency of the emission control systems of the other polymerization plants is less than the most efficient site and is of the order of 0.75%, then the VDC emissions from these operations could approach 262,000 pounds per year. Adding the 258,000 lbs. to this figure, it is estimated that 520,000 pounds of VDC are emitted per year from all polymerization sources.

All major polymerization companies report continuing efforts to improve the polymerization efficiency as a means of reducing the amount of unpolymerized monomer that must be stripped from a given batch. The installation of control equipment, such as condensers is always considered by the processor. However, most of them have noted that the cost of such installations for small capacity plants (less than 3 million pounds per year) can be prohibitive. This is particularly true if the site does not include other ethylenic type polymerization processes.

Polymerization processes are historically batch operations. Consequently, reactors, strippers and storage vessels must be cleaned periodically. The wash waters contain polymerized VDC, plus small quantities of VDC monomer. One source indicated that the PVDC content of the waste liquid stream represented about 6% of the VDC monomer polymerized. The residual VDC monomer in this waste stream was about 0.05% of the PVDC in the liquid waste. Another polymer manufacturer reported that about 1-1/2 to 2% of the PVDC polymer produced is sent to waste disposal.

All polymerization companies reported that liquid wastes are sent to waste control disposal areas. It is estimated that of the 135 million pounds of VDC polymerized each year, up to 8.1 million pounds of PVDC are sent to liquid waste disposal systems. About 4,000 pounds of monomer VDC are in the liquid wastes originating from polymer operations.

4.4 POLYMER CONSUMPTION PROCESSES

Polyvinylidene chloride is sold as a latex emulsion containing 50 to 63% solids, or as a dry resin. The polymer content of these resins typically contains 75 to 90% VDC, the balance being the comonomer.

PVDC latexes are used chiefly for coating packaging film substrates to improve their barrier properties and to provide heat sealing properties to the film. Among the films that are coated with this product are paper, polypropylene, nylon and polyester. The flame retardant property of VDC is utilized in those latexes in which the VDC content is less than 50%. Typical of this are latexes, prepared by copolymerizing 10 to 40% VDC with butadiene-styrene, to be used as a flame retardant, resilient backing for carpets.

Solid PVDC resin is used chiefly to extrude film, monofilament fiber, or pipe. A second use is in the preparation of a solvent solution for coating cellophane.

When VDC is copolymerized with 70 to 90% of acrylic monomer, the resultant polymer is used to manufacture modacrylic fibers, an acrylic fiber with improved flame resistivity.

4.4.1 Film Extrusion

PVDC film is extruded using both conventional flat die extrusion and blown film extrusion techniques.

The flat die extrusion process is often used as an inline unit which is part of a complete food packaging system. This technique is used for smaller extrusion lines.

The resin, purchased pre-blended in fiber drums, is fed to the extruder. The molten resin is then forced through a flat die to form a film. The film then moves to the packaging section where it is wrapped around the food item. Film scrap losses from this system can be as high as 50%.

Figure 4-5 is a representative flow diagram of the blown film process. It is identical to that used to extrude PVC, polyethylene and similar films. If a shrink film is desired, the blown film process is modified so that tension is applied to the blown film before it is completely cooled. This increases the molecular orientation of the polymer forming a "biaxially" oriented film.

As shown in Figure 4-5 the powdered resin is received either in 1,000 pound Gaylord containers, or in bulk hopper rail car. From here, the PVDC powder, which is an 85 to 90% copolymer with vinyl chloride, is fed to the compounding line where it is blended with a variety of additives, including stabilizers and plasticizers.

Mixing or compounding is carried out in a high intensity blender (i.e. a Banbury). The intense mechanical action in the blender develops sufficient heat to raise the temperature of the compounded plastic material to as much as 170°F (77°C).

From the Banbury mixer, compounded resin passes to the blown film extruder. If a biaxially oriented film is desired, a process is used in which the bubble, as it is formed, is subject to a stretching technique. The film is then "converted," i.e., slit to size and wound on rolls. Scrap losses as high as 25% are not uncommon as a result of the converting operation.

If the blown, stretched film is cooled rapidly, the resulting film has "shrink" properties. Upon reheating, it will shrink to its original unstretched condition.

In 1974, the powdered resin had a residual VDC monomer content of about 100 ppm. Since then, process improvements have reduced the residual monomer content of these resins to 20 ppm or less. The VDC monomer content in the preblended resin used in 1976

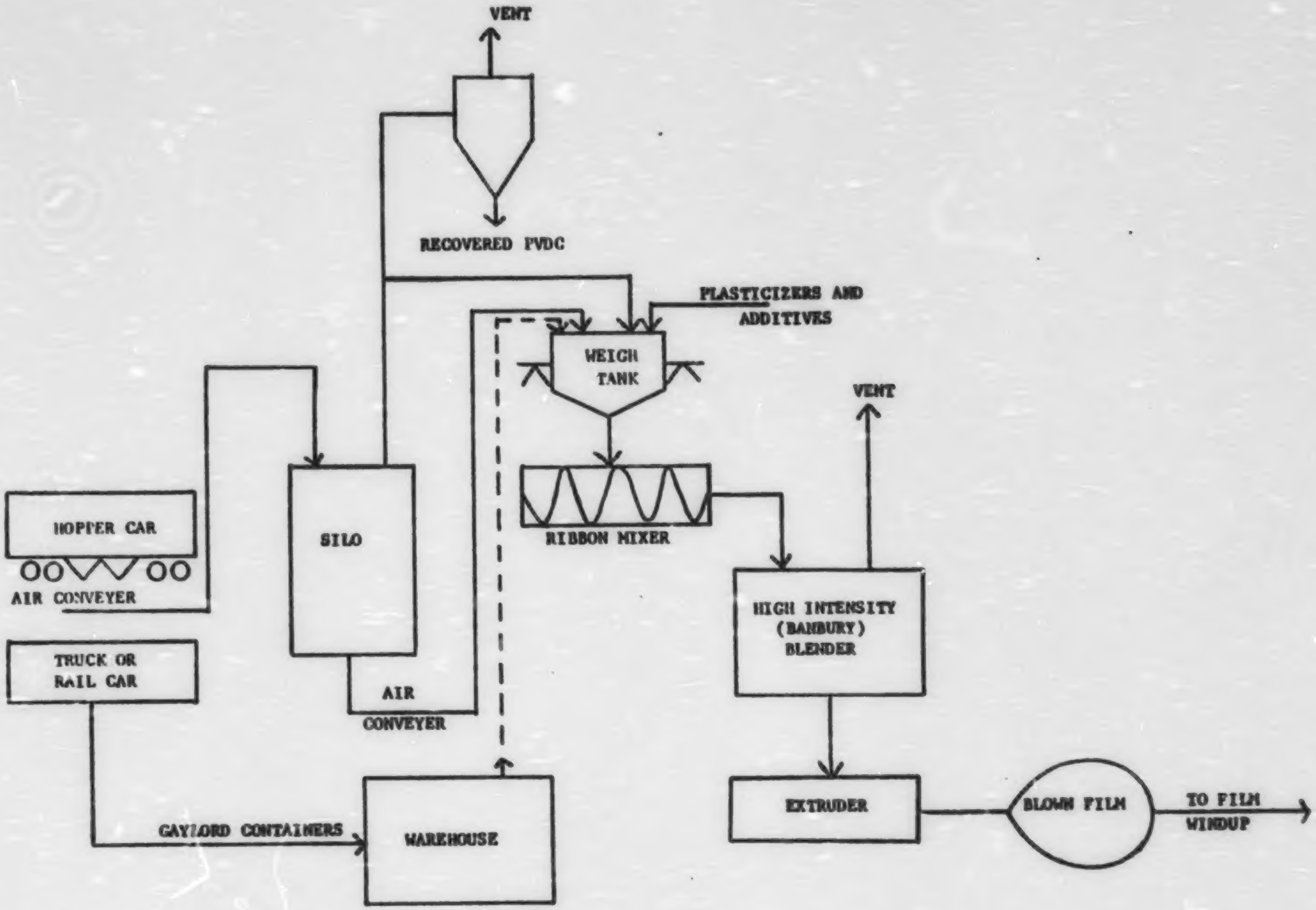

VENT
RECOVERED PVDC
PLASTICIZERS AND ADDITIVES
WEIGH TANK
VENT
HOPPER CAR
SILO
RIBBON MIXER
AIR CONVEYER
HIGH INTENSITY (BANBURY) BLENDER
TRUCK OR RAIL CAR
AIR CONVEYER
EXTRUDER
BLOWN FILM
TO FILM WINDUP
GAYLORD CONTAINERS
WAREHOUSE

Figure 4-5. Blown Film Process

by one extruder of flat film is reported to be below 7 ppm. In the blown film process, the residual monomer together with other fumes generated in the blender as a result of the mechanically generated heat, are vented to the atmosphere through an induced fan ventilation system connected to a hood stack over the mixer. These fumes contain some if not most of the VDC monomer residual in the purchased resin. With adequate ventilation of the blender, VDC levels in the plant environment are as low as 0.001 ppm.

In the smaller, flat die extrusion operations, the VDC monomer contained in the resin would be vented through the extruder. None of the film extruders treat the gases vented from the extrusion process.

Coextrusion is a new development in which a customized film may be made combining the mechanical and other properties of more permeable polymers with the high barrier properties of PVDC copolymers. Coextruded film permits the use of thin films of the expensive PVDC copolymer with outer layers of resins that are easier to process, more thermally stable and less expensive.

The process uses flat film extrusion techniques in which each polymer is extruded separately and combined using a calender plus, in most instances, an adhesive. Tubular coextrudates can also be made using those extruders to produce a five layered structure of polyethylene, glue, high barrier PVDC, glue and polyethylene (Leahy, 1976).

4.4.2 Coating Processes

There are two different methods of coating flexible films with PVDC. In one, the resin is dissolved in a suitable solvent to produce the coating "dope"; in the other, an aqueous emulsion latex is used. The aqueous emulsion latex is the more commonly used material for application of a PVDC barrier coating. The solvent coating method is used when the film to be coated is sensitive to water, such as cellophane.

4.4.2.1 Cellophane Coating

Cellophane is an example of a film coated from a solvent solution. A representative cellophane solvent coating operation is shown in Figure 4-6.

The polymer resin is received in 1,000 pound paperboard unlined Gaylord containers and stored until required. The polymer is taken from storage and fed into a mixing tank where it is dissolved in a suitable solvent (such as tetrahydrofuran). From the mixer, the lacquer is transferred to a closed, vented tank until ready to be used. The lacquer is pumped from storage to the roll coater where it is applied to the cellophane sheet. The coated cellophane film goes to the solvent removal oven, then to the humidifying oven and finally to wind-up.

All the equipment is enclosed and under a slight negative pressure. The indraft of air prevents emission of fumes into the plant operating area. The indraft air from the equipment is vented to a common header together with the exhaust air from the solvent removal oven. The exhausted air stream is blown through activated carbon adsorbers in which the solvent is removed and the solvent-free gases are vented to the atmosphere. The solvent is recovered by regeneration of the adsorber system, purified and returned to the process. The adsorbers are operated in such a way that any VDC monomer that might have been released during the coating and drying operation is at best only partially adsorbed. The majority probably "blows" through and is vented to the atmosphere.

The maximum quantity of VDC monomer that could be emitted at all the cellophane coating plants, based on a 20 ppm content in the polymer, would not exceed 360 pounds per year, or about one pound per day divided among the three coating locations (see Table 4-10).

4.4.2.2 Emulsion Coating

The great majority of flexible packaging film is coated using a latex emulsion, since the water base does not adversely effect the quality of the flexible film base. Because the PVDC

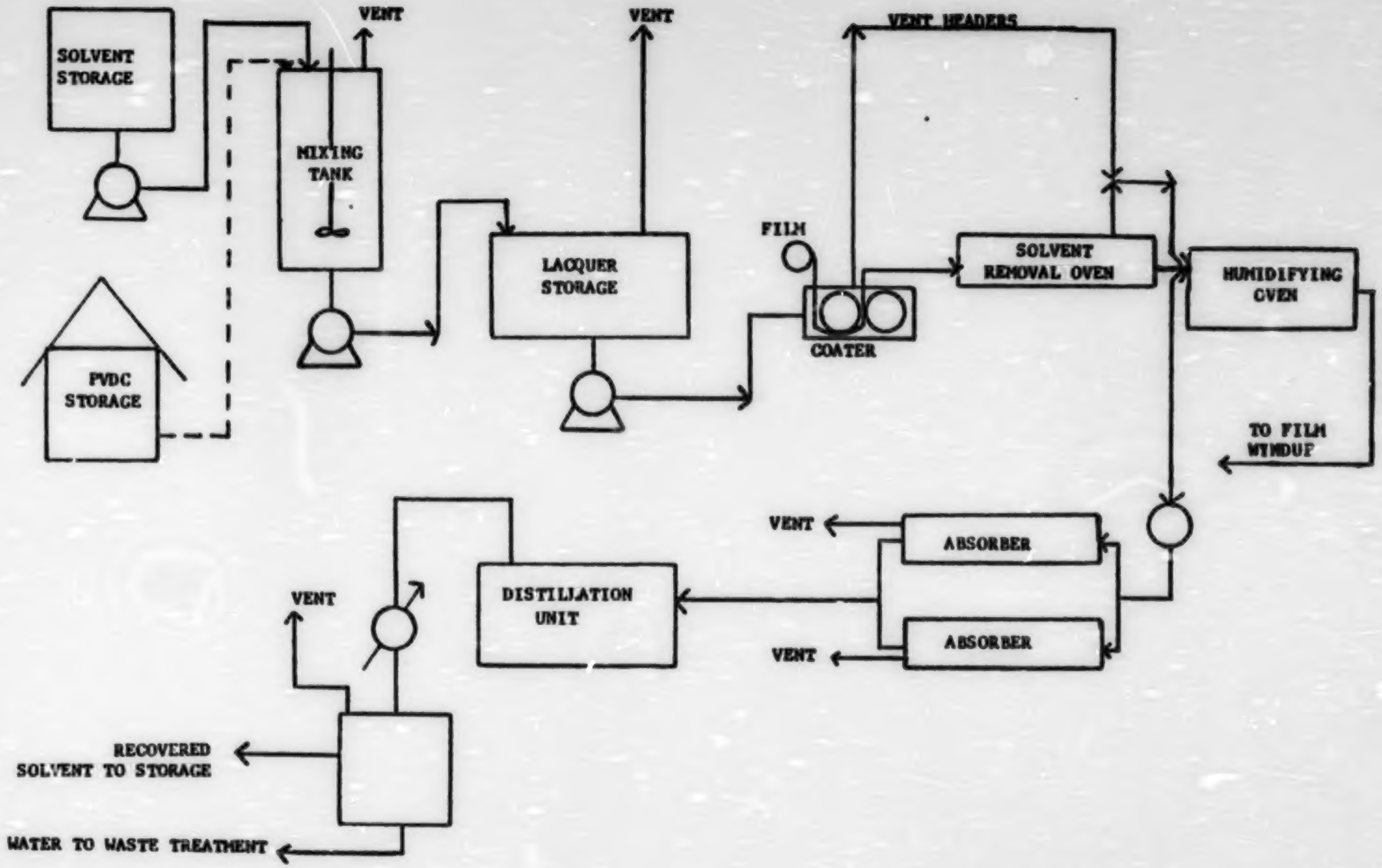

SOLVENT STORAGE
VENT
MIXING TANK
PVDC STORAGE
VENT
LACQUER STORAGE
FILM
VENT HEADERS
COATER
SOLVENT REMOVAL OVEN
HUMIDIFYING OVEN
TO FILM WINDUP
VENT
ABSORBER
VENT
ABSORBER
DISTILLATION UNIT
VENT
RECOVERED SOLVENT TO STORAGE
WATER TO WASTE TREATMENT

FIGURE 4-6. CELLOPHANE SOLVENT COATING PROCESS

latex used for coating packaging films is water based, they can be applied by almost any packaging film converter using standard coating machinery. The basic difference between a large and a small converting operation is the size and complexity of the machines. Most converters of packaging materials have coating equipment in their line. Hence they would find it easy to apply a PVDC coating to any substrate when required. Although there are a number of major convertors (see Table 4-2), there are an even larger number of small convertors that can coat paper or plastic film when they have orders.

The equipment used to coat flexible film consists of a roll coater to which is fed the latex and the film. Depending on the coater design the film may be coated on one or two sides. The coated film then passes to the dryer oven. It is in this apparatus that substantially all the residual VDC monomer contained in the latex will be released and vented to the air.*

Based on a residual monomer content in the latex product of 50 ppm, as reported by the major barrier latex producers, and an estimated consumption of approximately 30 million pounds in 1976, calculations indicate that only 1,500 pounds per year of VDC monomer are emitted by the more than 36 major converters.

4.4.3 Specialty Latexes

These latexes are usually copolymers of VDC with other monomers where the VDC content is less than 50%, typically 10 to 40%. VDC is used in these polymers for the flame retardant property that it imparts.

Representative of these latexes are those in which butadiene-styrene is copolymerized with VDC to produce a flame retardant elastomeric backing for carpets.

The process for using these latexes is common to the industry and consists of applying the latex, usually compounded with foaming agents as a relatively thick coating on the carpet. It then is conveyed to the curing and drying ovens.

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*Industry Sources.

It is our present understanding that little effort is made to control the emissions from this operation. Industry reports indicate that the VDC monomer content of the specialty latexes is less than 4 ppm, based on solids content. Based on the production of about 50 million pounds of these VDC-containing resins, it is estimated that the total amount of VDC monomer that could be emitted by carpet manufacturers would not exceed 100 pounds annually.

4.4.4 Environmental Management

Current polymerization technology permits the production of latexes with a VDC monomer content of less than 100 ppm, based upon dry solids. Most latex manufacturers currently report they are producing latexes with VDC monomer content on the order of 50 ppm. Resins used for extrusion or for solvent coating have VDC monomer contents on the order of 20 ppm.

These low levels of monomer for both classes of products have been achieved within the past two to three years. The manufacturers of PVDC latex report that they have been modifing their processes to effect reduction in VDC monomer content. They report, typically, reductions from a level of 600 ppm in 1971 to less than 50 ppm in 1976.

On this basis, total VDC monomer in the products sent to latex coaters can be calculated to be 1,500 to 2,000 pounds per year (based on 50 ppm content in 30 to 40 million pounds). This total quantity is released in varying amounts by over 40 establishments in all parts of the U.S.

Industry sources report that the rug backing latex as sold contains from 15 to 20 ppm of VDC monomer. Based on a current sales of about 40 million pounds of PVDC containing latex to the rug industry, the maximum VDC monomer emission loss at all the rug and carpet manufacturing plants is calculated to be 600 to 800 pounds per year.

The quantity of VDC monomer in the resins used by cellophane coaters is on the order of 320 pounds per year (an estimated 16 million pounds consumed with 20 ppm VDCM content) at three sites. Based on an estimated 80% loss of the residual VDC monomer content in the polymer, during coating and drying of the cellophane the VDC monomer content of the polymer on the coated cellophane is calculated to be approximately 4.0 ppm.

Extruded products, chiefly films, consume about 38 million pounds of VDC polymer resins annually. These resins contain a maximum of 20 ppm VDC monomer content as shipped. The amount of VDC monomer contained in the resins used for extrusion amounts to an estimated 760 pounds per year.

One industry source also indicated the sale in 1975 of an experimental polymer containing a total of 3222 pounds of VDCM residue. This material was used in perhaps 30 or so points in the U.S.

Information supplied by one source indicates that residual VDC monomer in finished PVDC containing products, e.g. saran fiber; extruded film; coated paper, plastic or cellophane film, is less than 2.5 pounds per million pounds of polyvinylidene chloride. Based upon a total production of about 120 million pounds of PVDC copolymers, the probable amount of VDC monomer in converted products sold in the U.S. is calculated to be of the order of 200 to 300 pounds.

In those cases where the coating operation is a normal part of a packaging converting line, the drying section is usually connected to an emission control unit. This unit may consist of an adsorbent or an incinerator. In these cases, any VDC monomer emission would be removed from the system effulent.

Estimated losses of VDC monomer from convertors are shown in Figure 4-7.

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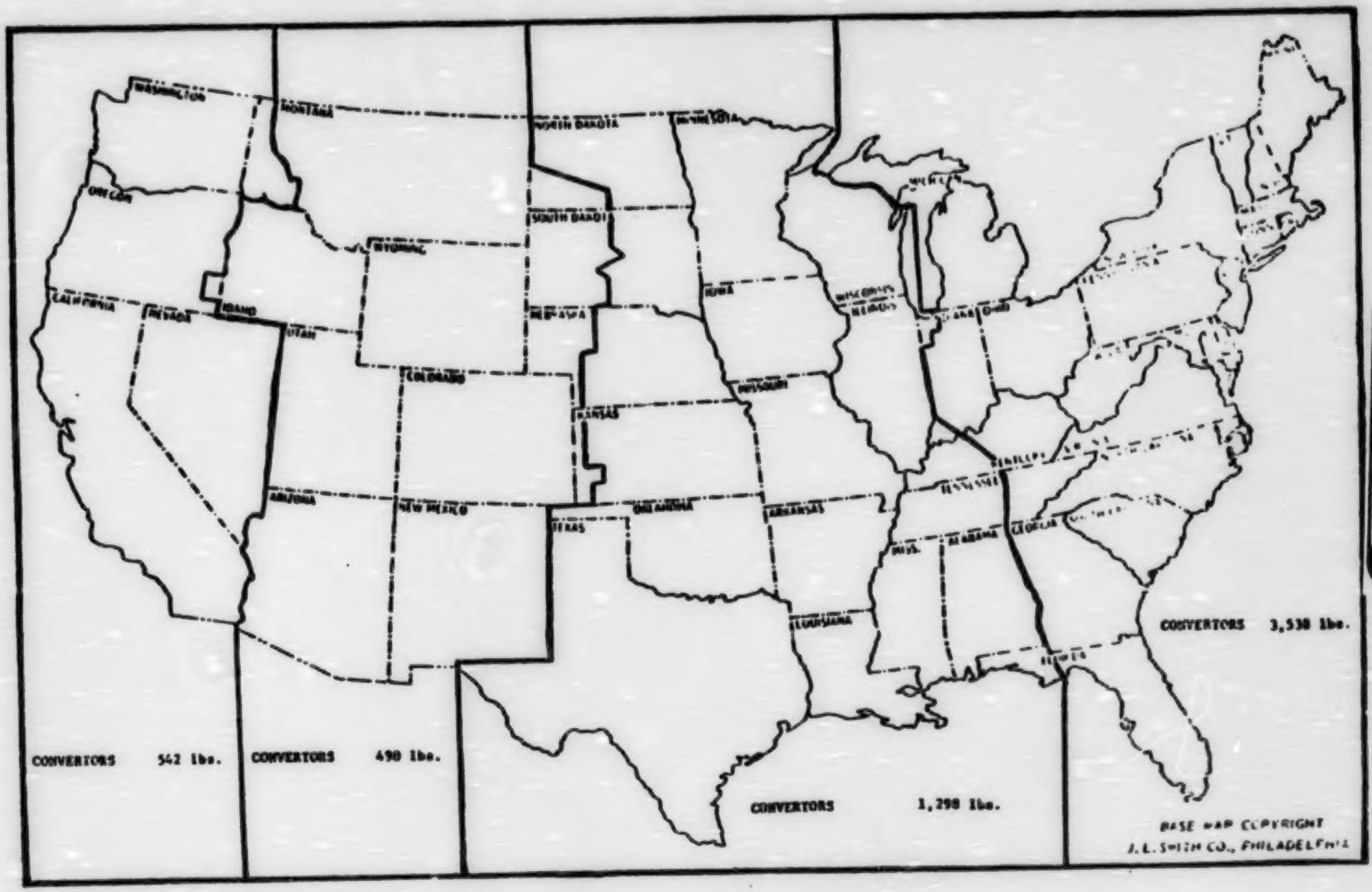
WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
OREGON
SOUTH DAKOTA
WYOMING
IOWA
WISCONSIN
MICHIGAN
CALIFORNIA
NEVADA
IDAHO
UTAH
NEBRASKA
ILLINOIS
INDIANA
OHIO
COLORADO
KANSAS
MISSOURI
ARIZONA
NEW MEXICO
TEXAS
OKLAHOMA
ARKANSAS
TENNESSEE
MISS.
ALABAMA
GEORGIA
LOUISIANA
CONVERTORS 542 lbs.
CONVERTORS 490 lbs.
CONVERTORS 1,298 lbs.
CONVERTORS 3,530 lbs.
BASE MAP COPYRIGHT
J.L. SMITH CO., PHILADELPHIA

Figure 4-7. Estimated Losses of VDC Monomer from Convertors in 1975
(Industry Sources, 1976)

Discussions with convertors revealed an awareness of the potential health and environmental implications of residual VDC monomer in the polymer resins purchased. The thrust of this concern has been directed more at obtaining resins from the polymerizers with the lowest possible monomer contents, than at implementing pollution control technology in their own converting operations. These pressures on the polymer producers appear to have had a direct impact as witnessed by the significantly lower levels of monomer achieved in both latexes and dry resins over the past two years.

4.5 MARKET STUDIES FOR VINYLIDENE CHLORIDE CONSUMPTION

Vinylidene chloride monomer has three major commercial uses.

(1) Synthesis of 1,1,1-trichloroethane
(2) Production of various polymeric compositions
(3) Intermediate for captive organic chemical synthesis

The production of vinylidene chloride is dependent on the market for the various products derived from it. This section will discuss past, present and future markets for the several products derived from vinylidene chloride. Major emphasis will be placed on the uses of VDC polymers since these have the widest dissemination in the economy and have the greatest potential for containing residual monomer.

4.5.1 1,1,1-Trichloroethane (Methyl Chloroform)

Production and sales data for 1,1,1-TCE are given in the annual reports on Synthetic Organic Chemicals - U.S. Production and Sales, published by the U.S. International Trade Commission (formerly U.S. Tariff Commission). This data is summaried in Table 4-4.

The average annual growth rate for production of 1,1,1-TCE has been about 10%. It is estimated (Lowenheim and Moran, 1975) that about 30% of the methyl chloroform produced in the United States is derived from vinylidene chloride. Based on this estimate, the amount of vinylidene chloride consumed to synthesize 1,1,1-TCE for the period 1966-1976 can be calculated and is shown in Table 4-5.

TABLE 4-4. PRODUCTION OF 1,1,1-Trichloroethane in Millions of Pounds

(U.S. International Trade Commission 1975-1977; U.S. Tariff Commission 1968-1974)

1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976
242.9	269.7	299.4	324.3	366.3	374.6	440.7	548.4	591.6	458.7	582.8

TABLE 4-5. CALCULATED CONSUMPTION OF VDC FOR 1,1,1-TRICHLOROETHANE PRODUCTION

MILLIONS OF POUNDS

1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976
52.9	58.8	65.2	70.7	79.8	81.6	95.9	127.4	128.9	99.9	127

TABLE 4-6. MANUFACTURERS OF 1,1,1-TRICHLOROETHANE
(Chemical Marketing Reporter, 1977)

Company	Plant	Capacity (millions of pounds)
Dow Chemical Co.	Freeport, Texas	450
PPG. Inc.	Lake Charles, La.	175
Vulcan	Geismar, La.	65

The manufacturers of 1,1,1-TCE and their estimated capacities are shown in Table 4-6. Based on the reported capacity for PPG's existing plant, maximum VDC consumption is calculated to be about 130 million pounds.

Industry opinion is that the consumption of vinylidene chloride used to manufacture 1,1,1-trichloroethane is perhaps 15 to 20% higher than the volume calculated in Table 4-5.

Future technology changes indicate that new plants will use processes that do not start with vinylidene chloride. Industry sources report that the new PPG plant expansion for 1,1,1-trichloroethane scheduled for operation in 1978, which will double its capacity to over 300 million pounds per year, will not be based on vinylidene chloride. The change in PPG's technology is believed to be related to the economics of their overall chlorinated hydrocarbon operation.

A full study of the 1,1,1-TCE market is not part of the scope of this study. There are several commercial routes for the manufacture of 1,1,1-TCE, and PPG's announced plant expansion is reported to use one of the alternate routes. Thus a study of the overall market growth of 1,1,1-TCE could contribute little to the understanding of the future impact of VDC on the environment.

4.5.2 Polymers of Vinylidene Chloride

Vinylidene chloride, because of its chemical structure (described in Section 2.3) has the ability to react with itself (polymerize) or with monomers of similar structure to form long chain polymeric materials.

The homopolymer VDC is used infrequently because it forms a crystalline, brittle material. When copolymerized with other monomers, these physical characteristics are modified and a number of useful products can be made.

Some of the monomers used in forming copolymers include:

- Vinyl Chloride
- Acrylic Acid
- Methacrylic acid
- Acrylonitrile
- Butadiene
- Styrene

Vinylidene chloride copolymers have three properties that contribute to their commercial usefulness:

- Barrier resistance to gases, chiefly oxygen, water vapor, odors, fats and oils
- Non-flammability, that enables it to impart flame retardant properties to other materials
- Chemical inertness

The principal commercial applications of vinylidene chloride copolymers are:

- As an extruded film for packaging
- As a barrier coating on various flexible film packaging materials
- To produce modacrylic fiber, a flame retardant textile
- Extruded to form a mono-filament fiber
- To produce a flame retardant backing on carpets
- To manufacture plastic pipe or as a liner for steel pipe

4.5.2.1 Extruded Film

Extruded PVDC film, commonly known as Saran, is used in food packaging. Because of its excellent barrier properties to moisture and oxygen, it is used extensively in packaging fresh meats, processed meats and cheese, frozen poultry, etc.

"Shrinkwrap" saran film is used where tight fit is needed to cover irregular objects. Non-shrink-wrap saran film finds general use for food packaging and storage. The uses of saran wrap are summarized in Table 4-7.

TABLE 4-7. COMMERCIAL APPLICATIONS OF SARAN WRAP

SHRINKWRAP	NON-SHRINKWRAP
Packaging fresh meat for shipment from the slaughter houses to the butcher	Packaging processed meat products
Packaging frozen fowl	Cheese products
Processed meat products	Fresh meat packages for sale in supermarkets and meat stores
Cookie dough	Household wrap

The major extruders of PVDC (Saran) film are shown in Table 4-8. All the producers of film listed, except Union Carbide Corp. use PVDC resin supplied by Dow Chemical Co. Union Carbide uses resin imported from its Japanese partner, Kureha.

TABLE 4-8. MAJOR EXTRUDERS OF PVDC FILM

Company	Plants
Dow Chemical Co.	Midland, Michigan
Cryovac Corp. (Div. of W.R. Grace)	Simpsonville, S.C. Cedar Rapids, Iowa Iowa Park, Texas
Dobekman (Div. of American Can Company)	Cleveland, Ohio
Oscar Mayer Co.	Madison, Wisconsin Sherman, Texas Los Angeles, Calif. Davenport, Ia. Chicago, Ill. Nashville, Tenn. Philadelphia, Pa.
Union Carbide Corporation	Centerville, Iowa

The market for commercial applications of Saran film has been increasing at a rate of over 10% per year until recently. Changes both in technology and in the growth patterns in the consuming industries indicate that this large growth rate may not be sustained.

A major technological innovation that will affect PVDC demand in the production of shrinkwrap film, is a change from the use of a relatively thick PVDC mono-layer film to a multi-layer laminate consisting of two layers of a poly-film (polyethylene, nylon or polyester) with a thin sandwich of PVDC film. The Dow tradename for this laminate is Saranex. The effect of this change will be a reduction of the demand for PVDC film resin to one-seventh its present consumption. However, since the phasing out of the monolayer film will be accomplished over the next five years, and the demand for film for meat and poultry is expected to increase at a 5 to 10% per year rate, the actual impact on PVDC resin consumption for commercial film will be slight.

The household wrap market is very competitive. Many materials compete for a saturated market. Among these are:

- Polyethylene
- Wax paper
- Aluminum foil
- Polyester
- Polyvinylidene chloride (Saran)
- Polyvinyl chloride

The growth rate for household wrap Saran film is very small and seems to follow the general growth of the population. This growth rate will not increase unless the price of Saran wrap drops to a more competitive level with respect to other films. The estimated VDC consumption by PVDC manufacturers is shown in Table 4-9.

TABLE 4-9. CURRENT PRODUCTION OF PVDC FILM
(Industry Sources, 1976)

Manufacturer*	Estimated VDC Consumption (1976) (millions of pounds)
A	10.8
B	6.3
C	6.0
D	11.6
Others	3.5
TOTAL	38.2

4.5.2.2 Barrier Coatings

Another major application of PVDC or Saran resin in food packaging is as a coating on a variety of other substrates to provide improved barrier properties. Among the substrate films coated are:

- Cellophane
- Paper and paper products (including glassine)
- Polyester
- Polypropylene
- Nylon
- Polyethylene

The markets for packaging film materials in the food industry are highly competitive. Price, printability, convertibility, packaging machine handling characteristics, and ability to withstand shipping and handling in the store all play a role in the selection of a film for packaging a given food product.

PVDC copolymers provide the greatest barrier resistance to diffusion of gases and vapors. Coating a less expensive, stronger film base with a thin layer of PVDC resin can produce a film with enhanced barrier properties at a lower cost than can be obtained by using a PVDC film or the less expensive film in sufficient thickness to provide the desired barrier properties.

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*The estimated consumption represents totals for each company and not individual site consumption data.

The Saran coated film market has been stable over the last few years despite fluctuations in demand for a given substrate. For example, use of polypropylene and polyester films in food packaging has increased dramatically in the last five to ten years. This has been at the expense of older, more conventional materials such as glassine and cellophane. Thus, while the paper product food packaging market has decreased, other plastic film markets have opened up in their place. In almost all cases, barrier properties are provided by Saran coatings.

Cellophane

The percentage of cellophane coated with PVDC has been increasing with respect to the total production of cellophane. However, overall cellophane production in the United States has been decreasing as it loses markets to other packaging films such as polyethylene and polypropylene.

The share of the cellophane market among the three producers is shown in Table 4-10.

The average weight of PVDC on cellophane is estimated to be 8-1/2%, based on an average coating weight of 3 gms/sq m. Industry sources estimate that approximately 18 million pounds of polyvinylidene chloride copolymer are currently being consumed for coating cellophane. The present consensus of the industry is that the projected consumption of polyvinylidene chloride copolymer for coating cellophane during the next five years will remain static or slowly decline.

Loss of non-food cellophane markets to other plastic films, chiefly polypropylene and polyester may be balanced by a proportionate increase in the use of saran coated cellophane for snack food packaging. Age of plants and increasing cost to manufacture cellophane will have a negative impact on the cost competitiveness of cellophane with plastic films.

TABLE 4-10. CELLOPHANE MARKET
(Industry Sources)

Company	Plant Location	% Share of Market
DuPont	Clinton, Iowa	40
FMC	Fredricksburg, Va. Philadelphia, Pa.*	35
Olin Corporation	Pisgah, N.C.	25
		100

*The Marcus Hook plant of FMC was closed in January, 1977. All production of FMC's coated cellophane will be done in the Fredericksburg plant.

The cellophane production in the U.S. is given in Table 4-11, with the estimated percentage that is coated with polyvinylidene chloride.

Paper Products, Glassine and Plastic Films

The primary application of PVDC emulsion latex is to provide barrier properties to paper, paper board, glassine, and plastic flexible film.

In contrast to cellophane coating which uses a solvent solution of PVDC resin, these flexible film substrates are coated using an aqueous emulsion latex. The coating process, using a water based emulsion latex, is non-hazardous (no solvent) and is compatible with typical packaging converting equipment that would include in its line a conventional roll coating unit. Consequently, the coating of the flexible film materials other than cellophane can be done in a large number of establishments. These range in size from those capable of consuming as much as 5 to 6 million pounds of PVDC per year, to those using as little as 40,000 pounds.

The emulsion copolymers used as barrier coatings contain between 75 and 90% vinylidene chloride, the balance consisting of vinyl chloride or acrylates. As discussed earlier, use of a PVDC copolymer coating upgrades less expensive forms of packaging material by providing them with improved barrier resistance to water vapor, gases, odors, oils and greases. Coating weights of from 3% to 20% are applied.

PVDC coated flexible films are used for packaging a variety of foods including candy, bread, cake, crackers, potato chips, meat, cheese, snack foods of all types, and cereals. Coated paper board stock is used for bottle caps, mayonnaise jar covers, etc. In addition PVDC coated papers are used for such non-food items as soap and cosmetics because of their barrier properties.

Estimates of the quantities of PVDC latex used for coating the various substrate films are shown in Table 4-12. The major coaters and their plant locations are shown in Table 4-13.

TABLE 4-11. PVDC-COATED CELLOPHANE PRODUCTION, MILLIONS OF POUNDS
(Modern Packaging Encyclopedia, 1975,
Industry sources, M. Sittenfield and
Associates, estimates)

	1970	1973	1974	1975	1976
Total Cellophane	340	325	335	270	300
Estimated % Saran coated	40%	52%	54%	54%	56 to 60%
Saran Consumption			16	12.4	18
VDC content in Saran (90%)			14.4	11.2	16.2

TABLE 4-12. CONSUMPTION OF VDC AS A LATEX COATING
(M. Sittenfield & Associates estimates)

SUBSTRATE	% SUBSTRATE COATED WITH PVDC	VDC CONSUMED (Millions of lbs.)
Glassine and Paper	60%	14
Paperboard	5%	1.6
Plastic Film (Polypropylene, Polyester, Polyethylene)	32%	8
Miscellaneous Materials	10%	3.2
TOTAL		26.8

It has been estimated that approximately four to five million pounds of polyethylene film are currently being coated annually, consuming between 400,000 and one million pounds of PVDC. Industry data indicate that currently 15 million pounds of polyester film, 30 million pounds of oriented polypropylene, and two million pounds of nylon film are being coated with PVDC. Based on reported coating weights of 20% on polyester, 10 to 15% on polypropylene and equivalent percentages on nylon, present PVDC consumption on these films is estimated at 3.0, 3.0 to 4.5 and 0.3 to 0.45 million pounds respectively.

Both PVDC coated polypropylene and PVDC coated polyester films are relatively new factors in the packaging field. As a result, demand for these coated materials is expected to grow at a relatively higher rate than the normal economic growth for the next five years as they take over older packaging film markets. It is expected that the growth will tend to slow to a rate in keeping with the general growth of the economy.

Polyester film markets in food packaging opened up at about the same time as polypropylene (mid-60's). Projected growth rate of PVDC coated polypropylene is estimated at 20% per year, while coated polyester is experiencing a somewhat slower growth rate,

TABLE 4-13 MAJOR PVDC LATEX BARRIER-COATING USERS

(Milgrom, 1976 and M. Sittenfield and Associates, 1977)

PAPER AND GLASSINE SUBSTRATE

COMPANY	PLANT LOCATION
Oneida Packaging Div. (Deerfield-Reed Corp.)	Clifton, N.J.
American Bag and Paper	Philadelphia, Pa.
Consolidated Paper	Wisconsin Falls Wis.
Crown Zellerbach	Portland, Oregon
Daniels	Rhinelander, Wis.
Diversa-Pak	St. Petersburgh, Fla.
Dixico	Dallas, Texas
DuPont	Circleville, Ohio
Milprint	Milwaukee, Wis.
Suretech Coating (Philip Morris)	Nicholasville, Ky.
Rexham	Memphis, Tenn.
Rhinelander (Div. of St. Regis)	Rhinelander, Wis.
Thilmany	Kaukauna, Wis.
Chase Bag Co.	Hudson Falls, N.Y.
Print Pak	Atlanta, Ga.

PAPERBOARD SUBSTRATE

Gordon Cartons	Baltimore, Md.
Green Bay Packaging	Green Bay, Wis.
Interstate Folding Box	Middletown, Ohio
Michigan Carton Co.	Battle Creek, Mich.
Olinkraft	W. Monroe, La.
Zumbril	Cincinnati, Ohio

PLASTIC SUBSTRATE

COMPANY	PLANT LOCATION	TYPE OF PLASTICS
DuPont	Circleville, Ohio	Polyester
Cryovac	Simpsonville, S.C.	Polyester
Minnesota Mining & Mfg.	Irvington, N.J. Decator, Ala.	Polyester
Allied Chemical Corp.	Pittsville, Pa.	Nylon
Hercules	Convington, Va.	Polypropylene
Milprint	Milwaukee, Wis.	Polypropylene
Cryovac	Simpsonville, S.C.	Polypropylene
Curwood, Inc. (Div. of Bemis)	New London, Wis.	Polyethylene
American Can Co.	Neenah, Wis.	Polyethylene
Standard Packaging	Clifton, N.J.	Polyethylene
Sealed Air Corp	Fairlawn, N.J.	Polyethylene

estimated at about 10% per year. Another newcomer to the barrier-coated packaging market is nylon. Less than two million pounds per year of nylon film are reported to be coated with PVDC resin. The specific use areas of PVDC coated nylon film have not been fully demonstrated.

The entire flexible packaging market is in a state of flux. There are many products that compete on the basis of price, performance, type of product to be packaged, availability, acceptance by the consumer and compatability with a company's existing converting and packaging equipment. Thus the choice of which film is to be used for a given application, as well as whether the film should have a barrier coating, is not made easily.

Many of the newer materials are replacing older ones. For example, polypropylene and polyester are replacing cellophane. A co-extruded polyethylene PVDC film sandwich is replacing coated polyethylene, PVDC mono-layer film and glassine. Industry sources report that, although some applications of PVDC coated film as a packaging material are increasing, others are static or decreasing. The net result is an average slow growth of PVDC consumption by the food and food products packaging industry of perhaps 3 to 5% per year. The growth rate is related to the general expansion of the economy and the change in consumer eating habits in the direction of increased snack and convenience food consumption. No new users for PVDC coated films are forseen that will result in a sharp increase in demand.

Probable consumption in 1987 of VDCM in the production of barrier coating polymers can be estimated to reach 45 million pounds.

4.5.2.3 Specialty Latexes

Specialty latexes are emulsion latexes that are not used as a barrier coating on packaging films and typically, contain between 20 and 40% vinylidene chloride (dry solids basis). They are used to provide fire retardant properties to the base polymer. The largest single use of vinylidene chloride is as a comonomer with such other monomers such as butadiene-styrene to produce a fire retardant carpet backing.

The producers of the specialty latex resins are shown in Table 4-14. Goodrich Chemicals' Avon Lake, Ohio plant ceased production in 1974.

TABLE 4-14. PRODUCERS OF SPECIALTY LATEX RESINS

Company	Site
Dow Chemical	Dalton, Ga. Midland, Michigan
Grace Chemical	Owensboro, Ky.
Reichhold Chemical	Cheswold, Del.
Rohm & Haas	Knoxville, Tenn.
National Starch & Chemical Corp.	Meridosia, Ill.
General Aniline & Film Corp.	Chattanooga, Tenn.

Industry sources report about 520 million pounds per year of latex are used as a rug and carpet backing. About 75% of this quantity has flame retardant components built into the formulation.

Flame retardancy can be built into the butadiene-styrene copolymer by the use of alumina, PVDC or a mixture of these materials. Approximately 10% of flame retardant carpet backing contains some PVDC. Based on an average VDC content of 30% and a solids content in the latex as sold of 50%, it is estimated that about 6 to 8 million pounds of VDC monomer are consumed for use in flame retardant carpet backing. If all of the fire retardant carpet backing market used PVDC exclusively, VDC sales could approach 80 million pounds, a ten-fold increase. Industry experts believe that the chance of reaching this level of demand for VDC within the next 10 years is remote. The growth of this market is not expected to exceed the general expansion rate of the U.S. economy. However, growth in the direction of PVDC capturing a greater share of the flame retardant rug backing market could occur if the cost of alumina compared to that of VDC increased and a more favorable cost effectiveness ratio resulted. Another boost to the use of VDC would develop if more stringent federal regulations concerning fire retardancy in rugs and carpets are promulgated, particularly for consumer market applications.

One company that produced VDC-containing carpet backing polymers reports that it has closed one of its two plants within the past year. One reason given was, that based on the current polymerization process and its pollution control technology, a further reduction of VDC emissions would have required excessive capital expenditures in the range of $500,000 to $1 million. This when combined with the high price and low demand of VDC-containing polymers compared to alumina filled products would have made the operation unprofitable. The company is now producing a flame retardant rug backing at this plant using alternate methods and materials and will continue to do so until the raw material cost becomes more favorable for VDC.

4.5.2.4 Textile Fibers

The textile fiber market is composed of two types: the extruded monofilament, and the modacrylic fiber.

Extruded Monofilaments

The extruded monofilament is manufactured by one company, Amtek Company of Odenton, Md. A solid PVDC resin similar to that used to extrude PVDC film is used in its manufacture. The market for this specialty fiber is small and relatively static. According to industry spokesmen, the demand is tending to contract chiefly because of high cost relative to other polymers such as polypropylene. Most is used in the chemical industry for filter cloths. It also finds some use where a flame retardant fiber is required combined with good outdoor aging properties.

Losses of VDC monomer at the extrusion plant are of the same order as those experienced by the film extrusion industry-less than 20 pounds per million pounds of product.

Production of this type fiber is estimated to consume 3 million pounds of VDC per year and a maximum of 100 pounds of VDC monomer per year are emitted during extrusion.

Modacrylic Fibers

The modacrylics are a modified acrylic fiber which are manufactured because of their flame retardant character. They are sold under the trade names of VEREL (Tennessee Eastman), and ACRILAN (Monsanto). These fibers are made by copolymerizing between 10 and 30% VDC monomer with acrylonitrile. They have been marketed for a number of years to satisfy the demand for non-flammable fabrics, mostly sleepwear, draperies and automobile upholstery.

Growth of the modacrylic market has been impeded by several factors. There has been slow development of mandatory government regulations concerning flame retardant undershirts, childrens' sleepwear, etc., and textiles produced with modacrylic fibers do not have a good "hand", do not dye well, and generally cost more. These fibers process poorly compared to other textile fibers.

There are two commercial developments that could restrict further the expansion of the modacrylic market. These include the use of flame retardant finishes on other fibers, such as Decloran, and the development of flame resistance in such other fibers as nylon and polyester. It is the consensus of industry spokesmen that sales growth of modacrylics will be slow. A possible increase in demand for the modacrylic fibers could develop if the flame retardant "Tris" (Tris 2,3-dibromopropyl phosphate TBPP) is removed from the market place because of its suspected carcinogenic potential. However, the current situation is such that given a choice between the deficiences of modacrylic fabrics, other flame retardant coated fibers, and no flame retardant quality, the consumer will choose the fabric that is (a) less expensive, and (b) more pleasing to the touch and eye.

Estimated U.S. consumption of modacrylic fibers is given in Table 4-15. In addition, there is some exportation of these fibers (chiefly to Canada) that represents about 15% of the U.S. consumption.

Industry sources conclude that neither more stringent federal regulations concerning flame retardancy for wearing apparel nor improvement in the physical characteristics of the fiber will materialize within the next five years. Hence, growth rate will be slow to moderate (perhaps 5 to 8% per year) with some surges due to changes in fashion (e.g. reintroduction of pile fabrics).

TABLE 4-15. U.S. CONSUMPTION OF MODACRYLIC FIBERS
(Industry Sources, 1976)
Millions of Pounds

	1971	1973	1976
Modacrylic Fiber Consumption	40	60	40-50
VDC Consumption (based on 20% VDC content)	8	12	8-10

4.6 TRANSPORTATION AND HANDLING OF POLYVINYLIDENE CHLORIDE 1,1,1-TRICHLOROETHANE (METHYL CHLOROFORM)

4.6.1 Transportation and Handling of Polyvinylidene Chloride

Because polyvinylidene chloride polymers are inherently flame-resistant, they are not considered hazardous for transportation and handling purposes. In the past, the amount of VDC monomer present in the final manufactured polymer might have represented a possible hazard. It has however become practice for most polymer manufacturers to strip their final product to the extent possible to remove residual VDC. Consequently, their customers, who are fabricators, have few problems with respect to VDC monomer in their facilities (Milgrom, 1976).

Polyvinylidene chloride is transported in drums, tank wagons or rail tank cars, and handled in a manner similar to other polymer latexes. According to the U.S. Coast Guard (1974) manual "all commercial latexes are shipped in a variety of concentrations in water depending on the particular polymer involved and the intended use of the latex. None are particularly hazardous except in fires where all coagulate to gummy flammable material." Because fires always constitute a hazard around chemicals, normal fire prevention measures should be taken. One of the products of PVDC incineration is phosgene. Therefore protective respiratory equipment and clothing may be needed in fighting a PVDC fire. Cooling water sprays can be used to wash down a small spill but major spills should be diverted from sewers and cleaned up with suitable disposal methods.

4.6.2 Transportation and Handling of (1,1,1-Trichloroethane) (Methyl Chloroform)

The Manufacturing Chemists Association (1976) in its Chemical Safety Data Sheet on methyl chloroform states that: "....although it is one of the least toxic of the chlorinated hydrocarbons, 1,1,1-trichloroethane vapors, in low concentrations, have anesthetic effects, and in high concentrations can have more serious results."

Reported cases (Kleinfeld and Feiner, 1966) of fatal concentrations of 1,1,1-TCE attained in confined spaces indicate that skilled management practices for handling and transportating the chemical must be followed.

4.6.2.1 Mandatory Regulations

Recent changes by the Materials Transportation Bureau, Department of Transportation, have resulted in the addition of 1,1,1-TCE to their Hazardous Material Table. Unlike vinylidene chloride, however, it is subject to packing regulations for air shipment only. A summation of these rules can be found in Table 4-16.

1,1,1-TCE is also regulated by the International Air Transport Association.

4.6.2.2 Voluntary Regulations

American Conference of Governmental Industrial Hygienists

The Threshold Limit Value (TLV) for 1,1,1-TCE set by the ACGIH in 1963 is 350 ppm or 1.93 mg/l (Stokinger, 1963). The TLV indicates the safe level of the solvent vapor if it is inhaled over a period of eight hours daily, five days/week. Patty, (1963) has recommended a TLV of 500 ppm, but according to Aviado, et al. (1976) an unacclimated person can detect 100 ppm and there is mild irration due to low concentrations. There seems to be no reason to change the TLV of 350 ppm.

American Industrial Hygiene Association (Toxicology Committee)

The American Industrial Hygiene Association (1964) publishes an evaluation of emergency exposure limits for various substances. The emergency exposure limits represent peak values of times exposure that should not be exceeded. The values for 1,1,1-TCE are as follows:

TABLE 4-16 RULES AND REGULATIONS FOR TRANSPORTING 1,1,1-TRICHLOROETHANE

(Department of Transportation, 1976)

Proper Shipping Name:	Methyl Chloroform
Hazard Class:	Other Regulated Material-A (ORM-A)
173.500(a)(1)	Defines an ORM-A as a material which has an anesthetic, irritating, noxious, toxic, or other similar property and which can cause extreme annoyance or discomfort to passengers and crew in the event of leakage during transportation.
	Labeling Requirements
172.101	No labeling is required.
172.316	The ORM-A designation must be placed on at least one side.
	Packaging Requirements
173.505(1)	Governs limited quantities of ORM materials and limits an ORM-A liquid to 1 pint/package.
173.510(a)	Governs large quantities (general requirements for ORM materials). (1) Each material must be offered for transportation and transported in compliance with Subpart B, C, and D of Part 172 of this subchapter and subpart A of Part 173. (2) For packagings of 110 gallon capacity or less, sufficient outage (ullage) must be provided so the packaging will not be liquid full at 130°F. (55° C.). (3) When a liquid or solid has an absolute vapor pressure exceeding 16 p.s.i. at 100°F. (38° C.), the primary packaging must be capable of withstanding the inside vapor pressure at 130°F. without leakage. (4) Any material classed as an ORM material, which may cause a hazard in transportation due to its reaction with water, must be packaged with either an inner or outer water proof packaging.
173.605(a)	Specific requirements for 1,1,1-Trichloroethane (Methyl Chloroform) when offered for transportation on a passenger-carrying aircraft.

TABLE 4-16 RULES AND REGULATIONS FOR TRANSPORTING 1,1,1-TRICHLOROETHANE (Continued)

(1) Wooden box with inside earthenware, glass, metal, or plastic packagings of not more than 2 gallons capacity each, with sufficient cushioning and absorbent material to prevent breakage and leakage.

(2) Fiberboard box with inside earthenware, glass, metal, or plastic packagings of not more than 1 gallon capacity each, with sufficient cushioning and absorbent material to prevent breakage and leakage.

(3) Metal drum of not more than 10 gallons capacity.

(4) Outside packaging with inside earthenware, glass, plastic, or metal packagings of not more than 4 fluid ounces capacity each, with sufficient cushioning and absorbent material to prevent breakage and leakage. The maximum amount that may be shipped in any one outside packaging is 5 gallons.

Maximum Net Quantity in One Package

Passenger Carrying Aircraft	10 gallons
Cargo Only Aircraft	55 gallons

Concentration		Emergency exposure limits, minutes
ppm	mg/l	
2500	13.500	5
2000	10.800	15
2000	10.800	30
1000	5.400	60

National Fire Protection Association

The National Fire Protection Association's fire hazard rating system has been described in Section 3.6.2. No fire or reactivity ratings are given for methyl chloroform, but a health hazard rating of two has been reported (Manufacturing Chemists' Association, 1972).

4.6.2.3 Handling Procedures and Hazards

Because of its relatively low toxicity, there may be a tendency for workers handling 1,1,1-TCE to regard it as completely safe, use it to excess or ignore spillage. The following points should be considered in training employees in the proper handling of this chemical.

Instructions for reporting to the proper medical authority and equipment supervisor should be detailed to the worker. Sound manufacturing plant management requires that workers be warned of unnecessary vapor inhalation and direct contact with liquid 1,1,1-TCE. Though they are not considered serious, various side effects may result from 1,1,1-TCE contact. These include (1) dermatitis, caused by prolonged daily contact, (2) eye irritation when splashed by the chemical, (3) sickness from ingesting large amounts of the liquid.

When conditions are sufficiently hazardous to require personal protective equipment these may take the following forms (Manufacturing Chemists' Association, 1976):

Eye protection	Goggles or face shields
Respiratory protection:	Self-contained breathing apparatus, airline masks, industrial canister-type gas masks, chemical cartridge respirators.
Head protection:	Hard hats or soft caps
Foot protection:	Safety shoes made of leather; overshoes made of neoprene may be worn over the leather safety shoes.
Body protection:	Wash thoroughly after any exposure. Protective clothing made of polyvinyl alcohol or neoprene.

One of the most hazardous operations involving the handling of 1,1,1-TCE is the cleaning and repairing of tanks and equipment. Tanks, equipment, pumps, lines and valves should always be drained and thoroughly flushed with water before being repaired. Electrical connections should be disconnected and the tank steamed to remove residual TCE and its vapors. Steam lines should be large enough to raise the tank temperature above the boiling point (74° C) of 1,1,1-TCE. The vapors in the steam effluent should be controlled so as to avoid air contamination in the work area in excess of the threshold limit value (350 ppm). The tank can then be cooled by filling with water and draining once or twice.

Tanks which have been steamed and flushed with water should then be purged with fresh air.

4.6.2.4 Transportation Methods

1,1,1-Trichloroethane can be shipped in drums, rail tank cars, or tank wagons (Lowenheim and Moran, 1975). Examples of usual shipping containers are presented below (PPG, 1968).

DRUMS

54-Gallon at 77°F Drum - Lithographed

Steel, DOT 17E, 55 gallons, 2" and 3/4" bungs in head diametrically opposite; two rolling hoops; phosphatized interior; green and white lithographed exterior.

54-Gallon at 77°F Drum - Black

Steel, DOT 17E, 55 gallons, 2" and 3/4" bungs in head diametrically opposite; two rolling hoops; phosphatized interior; black enameled exterior. Carload orders for drums can be loaded in DF Hydro-Cushion cars where the maximum load is approximately 100 drums in 50' car. For tank wagons, maximum load is approximately 65 drums.

RAIL TANK CARS

Single Compartment

Car Size	Filled Net Weight	Length	Maximum Height	Width
4,000 gal.	22 Tons	35' 9"	12' 1"	9' 9"
8,000 gal.	43	41' 3"	14' 0"	10' 6-1/2"
10,000 gal.	54	41' 2"	14' 7-1/2"	10' 7-1/2"
20,000 gal.	105	48' 5"	15' 1/2"	10' 6-1/2"

Multiple Compartment

In addition to the single unit cars, there are compartmented cars available: a two compartment, 6,000 gallon car (3,000 gallons each), and a three compartment, 8,000 gallon car (2,700 gallons each). Each compartment has its own dome, internal valve, and outlet.

Tank Wagons

"Dedicated service" tank wagons are available in stainless steel or aluminum. For low-stabilized grade, stainless steel only. They can be equipped with pump, hose, or nozzles.

Maximum Load Limit

Bulk shipments are governed by local weight restrictions and available equipment.

The manufacturer and the shipper should be consulted for details on proper unloading procedures for drums, rail tank cars and tank wagons filled with 1,1,1-TCE. Manufacturing Chemists' Association (1976) has prepared a general guide for these procedures.

4.6.2.5 Storage Methods

It is important to maintain properly ventilated areas when storing 1,1,1-trichloroethane. Containers should not be located near open flames, open electrical heaters or high temperature operations because on exposure to high temperatures, the vapor may decompose to toxic and corrosive substances (see Section 2.4.2). As is the case with all chemicals, storage selection should be in accordance with local codes or authorities.

Steel is the most common construction material used for 1,1,1-TCE storage, but in facilities where excessive moisture occurs, resin linings or stainless steel may be preferred. Indoors, drums of 1,1,1-TCE may be stored in a cool place with the bung (stopper) up. Because there is a possibility water may be sucked in through the bung, drums may be stored horizontally outdoors. In all instances, drums should not be stored in pits, depressions, or basements.

The Manufacturing Chemists Association (1976) recommends the following storage procedures for 1,1,1-TCE stored in tanks. Whether tanks are placed vertical or horizontal, they should have a top and bottom manhold of at least 22 inches in diameter, in addition to filling, vent and measuring device openings. A two inch or two and one-half inch bottom outlet should be provided for use as a drain during clean-out operations. Vertical tanks should be of the closed top design, with the top welded vapor-tight. Each storage tank should have a vent to permit the escape of vapor during filling. Vents from indoor tanks should terminate outdoors in such a location so as not to contaminate work space air.

4.6.2.6 Accident Procedures

Although 1,1,1-TCE has no flash point or fire point, a high energy source may ignite high concentrations of the vapor in air (PPG,1968). Though this possibility is unlikely, if a fire does occur, then carbon dioxide, dry chemical agents or foam may be used to control it.

Spills should be cleaned up immediately by persons wearing protective equipment. Cleaning materials wet with 1,1,1-TCE should be placed in closed containers or dried outside. Clothing impregnated with 1,1,1-TCE should be immediately removed and then dried out-of-doors.

4.6.2.7 Disposal Methods

Current disposal methods in common use are those established by the Manufacturing Chemists Association (1976). They recommend that 1,1,1-TCE contaminated discharge water be air blown for a few hours in a well ventilated area. Limited amounts may be poured on dry sand, earth or ashes at a safe distance from occupied areas and allowed to evaporate into the atmosphere. These recommendations are superceeded by any local or state regulations concerning waste disposal to streams, municipal treatment plants or into the ground.

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SECTION V. USE ALTERNATIVES FOR VDC AND ITS END PRODUCTS

5.1 INTRODUCTION

Vinylidene chloride has been in extensive commercial use since 1939, when copolymerization and plasticization techniques were developed by workers at Dow Chemical Co. The resultant copolymers, known as saran or polyvinylidene chloride, have been produced continuously since that time.

Alternate raw materials and processes exist for the consumption of VDC in 1,1,1-TCE manufacture, and will have completely displaced VDC in this use by 1980.

A number of other polymers can substitute for saran in its applications as a packaging film or barrier coating. None, however, possess the same barrier resistance to both oxygen and water vapor for a given film thickness.

For the manufacture of flame retardant fibers, alternate materials for PVDC containing polymers exist, and more are in the developmental stages. The alternative material used as a replacement for PVDC in producing a flame retardant carpet backing has inferior physical and wearability characteristics.

5.2 1,1,1-TRICHLOROETHANE

Of the three companies currently producing 1,1,1-TCE (Dow Chemical Co., and PPG, Inc., and Vulcan), only PPG produces it from vinylidene chloride. The other production routes are:

(1) Chlorination of vinyl chloride

(2) Direct chlorination of ethane or ethylene

The specific process used by any of the 1,1,1-TCE producers, including PPG's hydrochlorination of vinylidene chloride, is dependent upon the company's desired product mix and economics of the overall chlorinated hydrocarbon operation.

5.2.1 Production Alternatives

In the first alternative, 1,1,1-TCE is derived from chlorination of vinyl chloride, which has been synthesized from ethylene dichloride, in turn derived from chlorination of ethylene or ethane. The second alternative results from the continuous non-catalytic chlorination of ethane and produces a variety of chlorinated hydrocarbons, including ethyl chloride, ethylene dichloride, vinyl chloride, vinylidene chloride, and the trichloroethanes. The producer can separate the various products and use them as is, or recycle them for further chlorination e.g., vinyl chloride to produce 1,1,1-TCE. The specific composition of the product ranges are considered proprietary, and depend on the temperature, catalyst and reaction time.

Thus, neither the various raw materials nor the processes discussed above can be considered true alternatives. The raw materials are all interrelated and the production processes use equivalent technology.

PPG will have phased out its 1,1,1-TCE plant using VDC by 1980 with an alternate process probably using ethylene dichloride or vinyl chloride. Hence, "alternatives" will have replaced VDC as the starting point for the production of 1,1,1-TCE within the next three years.

5.2.2 End Use Alternatives

The major use of 1,1,1-TCE is as a metal degreaser, in a wide range of industrial and commercial applications. In this regard, it is already functioning as the alternative to other solvents such as trichloroethylene because it is a non-flammable and a more chemically inert compound.

A major factor in its being the chemical of choice as a degreasing solvent is its relative lack of reactivity in the vapor state with atmospheric constituents. It is much less likely to form the peroxides, smog, and other pollutants which are a frequent by-product of the presence of unsaturated hydrocarbons in the atmosphere.

5.3 POLYMERS OF VINYLIDENE CHLORIDE

Vinylidene chloride is always used commercially with other monomers, to produce a range of plastics with varying properties and uses. The major comonomers used in the polymerization of VDC are vinyl chloride, acrylic acid, methacrylic acid, acrylonitrile, butadiene and styrene.

5.3.1 Alternative Chemicals and Processes

The main properties, for which VDC copolymers find a market, are barrier resistance and flame retardancy. VDC itself is the alternate chemical added to the copolymer mix to achieve a desired property. Thus, there are no alternatives to VDC for its specific applications in polymerization.

The polymerization processes used to manufacture VDC copolymers are of two main types: emulsion, and suspension polymerization. Both processes use essentially the same equipment and overall reactions, differing only in the reaction parameters, degree of conversion, and stripping techniques. Suspension polymerization commonly yields a latex, but it can also be used to produce the dry resin. Copolymerization with acrylic monomers to form modacrylic fibers uses the emulsion process.

The latex suspension process is not as widely used as the emulsion process, although some industry sources report that the suspension process is easier to control and results in fewer lost batches. However, the emulsion resin offers superior physical characteristics, in that the resin particles are smaller and the polymer extrudes and blends more easily.

The trends in alternate PVDC process technology are in the direction of improving the characteristics of the polymer produced, increasing degree of conversion of monomer, and reducing losses. New catalysts are being evaluated which would yield a suspension resin with the more desirable physical characteristics of the emulsion resin. The impetus for this new technology stems from the higher VDC monomer losses associated with the emulsion process, in terms of both sewered effluent from bad batches and monomer emissions from the process.

Alternate process technology for polymerization is aimed at increasing the amount of conversion of VDC into polymer without affecting the properties desired in the end product. This will reduce the amount of VDC monomer to be removed by stripping, as well as reducing the amount of residual monomer in the polymer.

5.3.2 End Use Alternatives

End use alternatives exist for all four major consumption areas of VDC copolymers. However, all have some drawbacks, either in terms of loss of specific desired properties in the end product, or the cost or quantity of alternative substances that would have to be used to achieve the same effect.

5.3.2.1 Alternatives to Saran Film

In contrast to other polymers, or copolymers of vinyl chloride, saran copolymers require very little or no added plasticizer to yield a flexible film. This characteristic is significant since the addition of plasticizers tends to destroy the barrier properties of the polymer films. The formulation chosen for a saran film is always a compromise between the barrier requirements and the physical characteristics, such as cling, clarity, machinability and printability, required by the film (Leahy, 1976).

Saran's unique characteristic is its outstanding barrier to transmission of both oxygen and water vapor. Other flexible polymeric films may possess similar barrier properties for either oxygen or water vapor, but not both. Table 5-1 compares oxygen and water vapor transmission rates for common commercial packaging films, all at 1 mil thickness and room temperature.

TABLE 5-1. TRANSMISSION RATES FOR PLASTIC FILMS
(Leahy, 1976)

	Transmission Rate	
Material	Oxygen*	Water Vapor**
Saran	1	0.2
Polyethylene	400	1
Polypropylene	245	0.5
Polyvinylchloride	25	5
Polyester	5	1.8

---

*units are cc/100 sq. in./day
**units are gm/100 sq. in./day

From this table it can be seen that polyethylene, polypropylene or polyester could replace saran, depending on the particular barrier properties required for a given application. Similarly, increased thickness of the other films could approach the barrier properties of the thinner saran film.

Another important alternative to the monolayer saran is the coextruded laminate film. In these flat film structures saran is sandwiched between polyethylene or other polyolefin skins. These laminates have outstanding physical properties, combining the flexibility, heat-sealability and low temperature properties of polyethylene with the barrier resistance of saran itself. A possible future advantage to the laminate may be that it isolates the saran from contact with the food. Until the question of the alleged migration of VDC monomer from saran into foods has been resolved (Chemical and Engineering News, 1977), this substitute for saran could prove to be of even greater commercial significance.

5.3.2.2 Alternatives to Saran-Coated Substrates

Coating of cheaper substrates, such as cellophane, or films with other desirable physical properties, such as polyethylene, with saran brings about a dramatic barrier improvement in the properties of the original substrate. Table 5-2 compares the barrier properties of various saran-coated and uncoated substrates.

Thus, depending on the nature of the food being packaged and the nature of the barrier resistance required, alternatives to saran-coated substrates could be selected. Again, the coextruded saran laminate provides an attractive alternative in terms of overall desirable physical characteristics, but it is not cost competitive with some of the cheaper substrates.

5.3.2.3 Alternatives to PVDC Latex Rug Backings

VDC is used as a comonomer with butadiene-styrene to provide flame retardant properties to the base polymer. Flame

TABLE 5-2. BARRIER PROPERTIES OF SARAN-COATED FILMS
(Roth, 1976; Modern Packaging Encyclopedia, 1975)

	Transmission Rate	
Material	Water Vapor*	Oxygen**
Cellophane, Uncoated	High	Variable
Cellophane, Saran Coated	0.4	0.2
Polyester, Uncoated	1	3
Polyester, Saran Coated	<.1	0.6
Polypropylene, Uncoated	0.25	150
Polypropylene, Saran Coated	0.25	<1
Nylon, Uncoated	High	2
Nylon, Saran Coated	0.5	0.5

---

*gm/100 sq in/day/mil
**cc/100 sq in/day/mil

retardancy can be built into the latex by the use of alumina, PVDC, or a combination of these materials. Only the PVDC acts as a functional additive. The VDC monomer forms part of the latex polymer molecule and thus adds to its elastomeric character. Alumina is heavy and when added in quantities sufficient to "quench" flame, it produces a cracky material with poor physical and wear properties.

Other flame retardants, such as the aryl phosphates are not suited to the latex plastics because they act as diluants, to separate polymer chains and provide "slip", rather than being incorporated into the molecular structure.

The use of Dechlorane +25 and decabromobiphenyl oxide as flame retardant melt additives for nylon carpets has also been reported (Stoddard, 1975). In this application the flame retardant material is blended into the polymer just prior to yarn formation, rather than formulated with the backing material.

5.3.2.4 Alternatives to Modacrylic Fibers

Modacrylic fibers are manufactured for the market for non-flammable fabrics, mainly sleepwear, draperies and automobile upholstery. Alternatives to the modacrylics include the use of flame retardant finishes on other fibers, such as Dechlorane. Work is also being done in the development of flame resistance in other fibers which currently enjoy greater popularity in the consumer market, such as nylon and polyester.

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SECTION VI. OVERALL MATERIALS BALANCE

6.0 OVERALL MATERIALS BALANCE

Vinylidene chloride is manufactured chiefly by the dehydrochlorination of 1,1,2-trichloroethane, or as a co-product of the reaction of ethane and ethylene with chlorine. It is not obtained from natural sources, nor is it accidentally produced in a natural environment.

Vinylidene chloride is consumed by

(1) Further chemical reaction to form other chemicals

(2) Polymerization with other monomers to form long chain thermoplastic polymeric materials.

During the production of vinylidene chloride, and in its conversion to other chemicals or polymers, there are losses of VDC to the environment as well as residual monomer remaining in the products derived from it.

Figure 6-1 is a flow diagram tracing the Input-Output balance of vinylidene chloride monomer from its manufacture through its consumption in various products to its conversion into end use materials.

6.1 VINYLIDENE CHLORIDE MANUFACTURE

Approximately 270 million pounds of vinylidene chloride were produced in 1976. Of this, estimated losses to the environment were calculated to be 550,000 lbs.

Of the balance, 130 million pounds were reported to be reacted to produce 1,1,1-trichloroethane: an estimated 5 million pounds were converted to a chemical intermediate, chloroacetyl chloride; the balance was co-polymerized with other monomers to produce VDC-containing polymers.

Figure 6-2 represents the output of VDC according to the percent consumed or lost.

6.2 VINYLIDENE CHLORIDE CONSUMPTION

6.2.1 VDC Consumption in Manufacture of 1,1,1-Trichloroethane

According to PPG, the sole manufacturer of 1,1,1-TCE from VDC, the conversion of VDC to 1,1,1-TCE is 100%, with no process losses of VDC to the environment occurring. There is some contamination of the 1,1,1-TCE produced with VDC monomer. This is reported to be about 100 ppm or about 17,500 lbs. per year.

The loss of this amount of VDC occurs at the very large number of sites where 1,1,1-TCE is used. It probably is lost chiefly by vaporization of 1,1,1-TCE during its transfer, use and recovery.

6.2.2 VDC Consumption in Manufacture of Chloroacetyl Chloride

This chemical is manufactured for captive use by Dow Chemical Co. They report no losses of VDC to the environment during

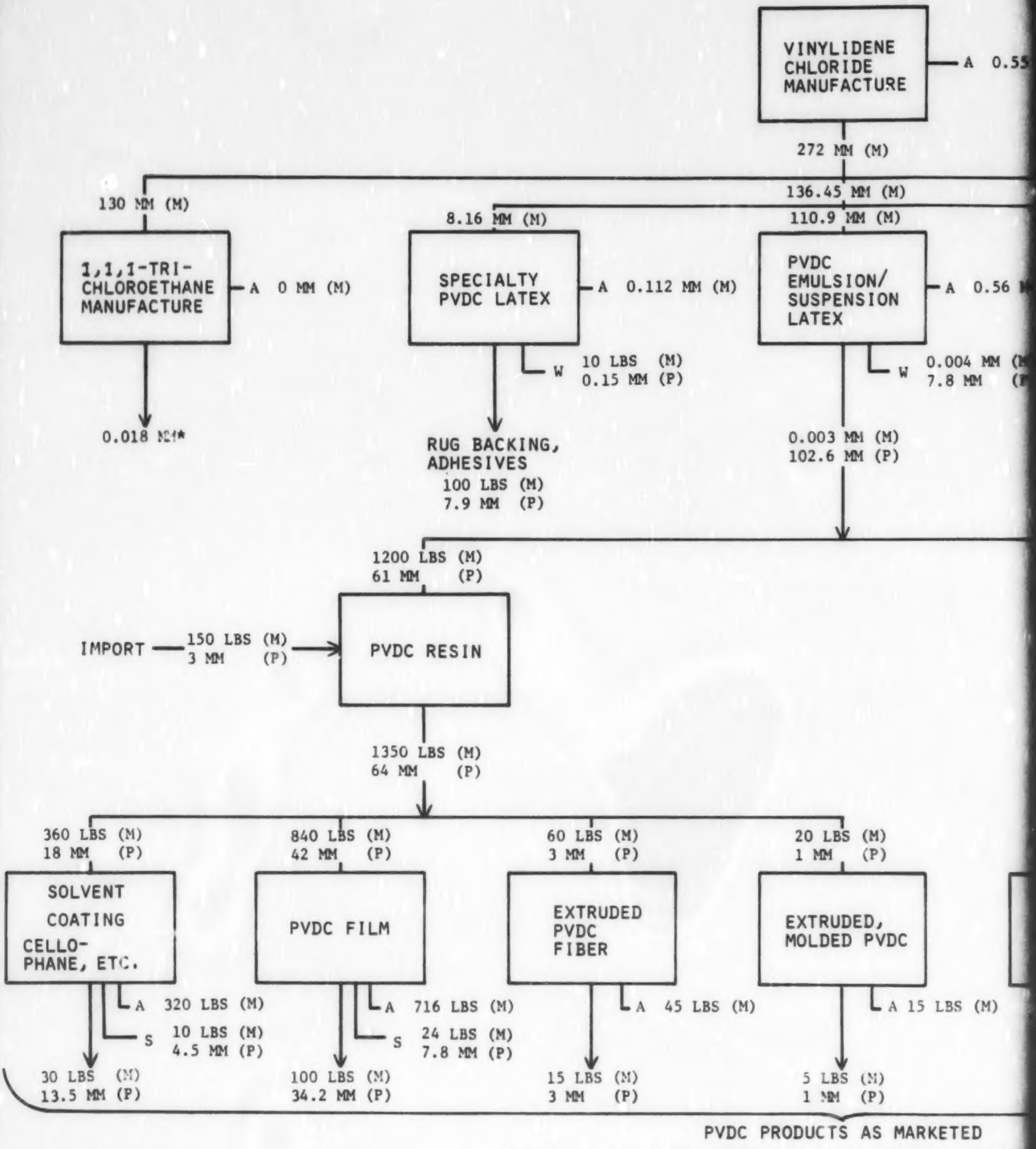
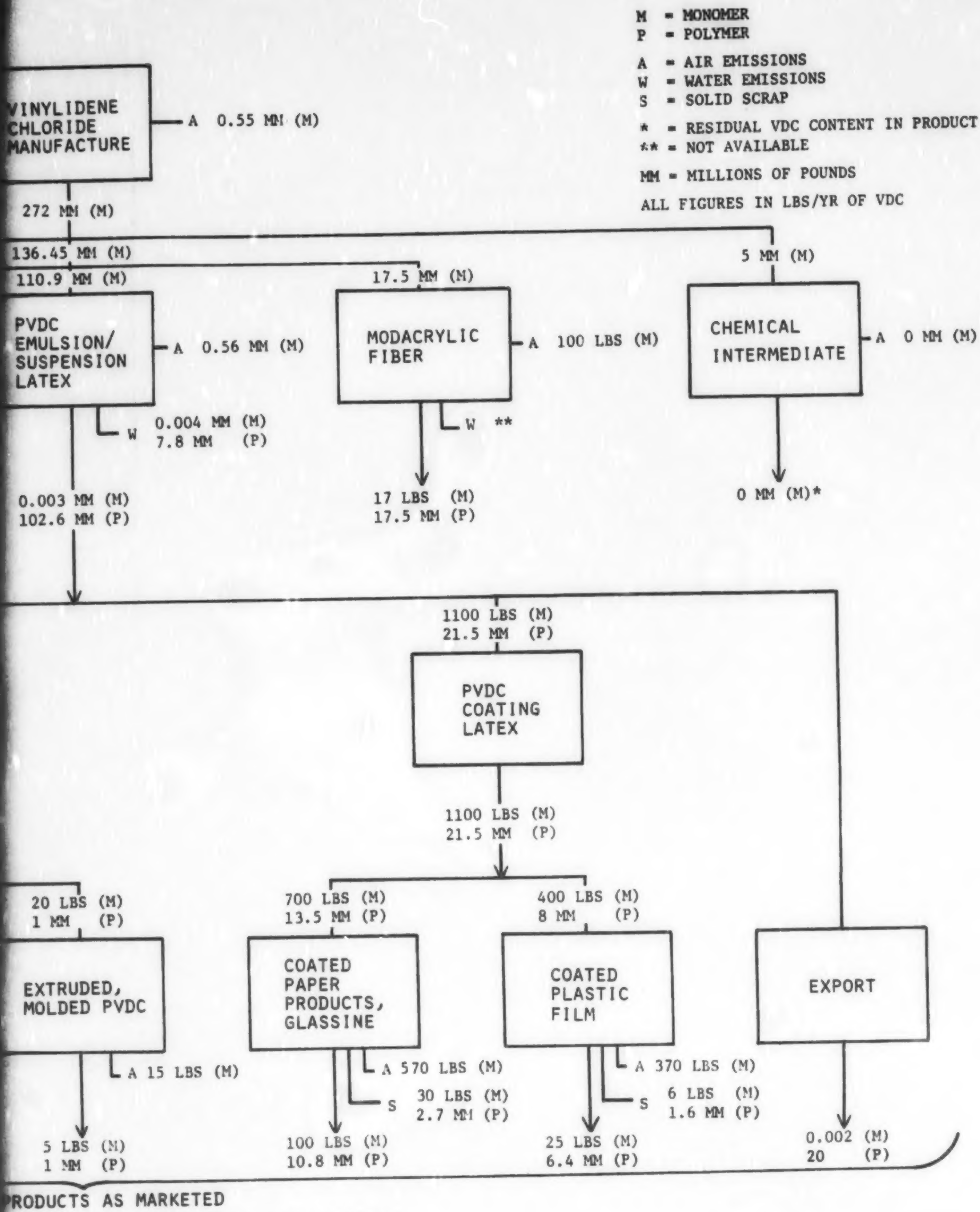

VINYLIDENE CHLORIDE MANUFACTURE
A 0.55
272 MM (M)
136.45 MM (M)
130 MM (M)
8.16 MM (M)
110.9 MM (M)
1,1,1-TRICHLOROETHANE MANUFACTURE
A 0 MM (M)
0.018 MM*
SPECIALTY PVDC LATEX
A 0.112 MM (M)
W 10 LBS (M)
0.15 MM (P)
RUG BACKING, ADHESIVES
100 LBS (M)
7.9 MM (P)
PVDC EMULSION/ SUSPENSION LATEX
A 0.56
W 0.004 MM
7.8 MM
0.003 MM (M)
102.6 MM (P)
1200 LBS (M)
61 MM (P)
IMPORT
150 LBS (M)
3 MM (P)
PVDC RESIN
1350 LBS (M)
64 MM (P)
360 LBS (M)
18 MM (P)
840 LBS (M)
42 MM (P)
60 LBS (M)
3 MM (P)
20 LBS (M)
1 MM (P)
SOLVENT COATING CELLOPHANE, ETC.
PVDC FILM
EXTRUDED PVDC FIBER
EXTRUDED, MOLDED PVDC
A 320 LBS (M)
S 10 LBS (M)
4.5 MM (P)
A 716 LBS (M)
S 24 LBS (M)
7.8 MM (P)
A 45 LBS (M)
A 15 LBS (M)
30 LBS (M)
13.5 MM (P)
100 LBS (M)
34.2 MM (P)
15 LBS (M)
3 MM (P)
5 LBS (M)
1 MM (P)
PVDC PRODUCTS AS MARKETED

FIGURE 6-1. VINYLIDENE CHLORIDE INPUT-OUTPUT


M = MONOMER
P = POLYMER
A = AIR EMISSIONS
W = WATER EMISSIONS
S = SOLID SCRAP
* = RESIDUAL VDC CONTENT IN PRODUCT
** = NOT AVAILABLE
MM = MILLIONS OF POUNDS
ALL FIGURES IN LBS/YR OF VDC
VINYLIDENE CHLORIDE MANUFACTURE
A 0.55 MM (M)
272 MM (M)
136.45 MM (M)
110.9 MM (M)
17.5 MM (M)
5 MM (M)
PVDC EMULSION/ SUSPENSION LATEX
A 0.56 MM (M)
W 0.004 MM (M) 7.8 MM (P)
0.003 MM (M) 102.6 MM (P)
MODACRYLIC FIBER
A 100 LBS (M)
W **
17 LBS (M) 17.5 MM (P)
CHEMICAL INTERMEDIATE
A 0 MM (M)
0 MM (M)*
1100 LBS (M) 21.5 MM (P)
PVDC COATING LATEX
1100 LBS (M) 21.5 MM (P)
20 LBS (M) 1 MM (P)
700 LBS (M) 13.5 MM (P)
400 LBS (M) 8 MM (P)
EXTRUDED, MOLDED PVDC
A 15 LBS (M)
5 LBS (M) 1 MM (P)
COATED PAPER PRODUCTS, GLASSINE
A 570 LBS (M)
S 30 LBS (M) 2.7 MM (P)
100 LBS (M) 10.8 MM (P)
COATED PLASTIC FILM
A 370 LBS (M)
S 6 LBS (M) 1.6 MM (P)
25 LBS (M) 6.4 MM (P)
EXPORT
0.002 (M) 20 (P)
PRODUCTS AS MARKETED

CHLORIDE INPUT-OUTPUT FLOW DIAGRAM

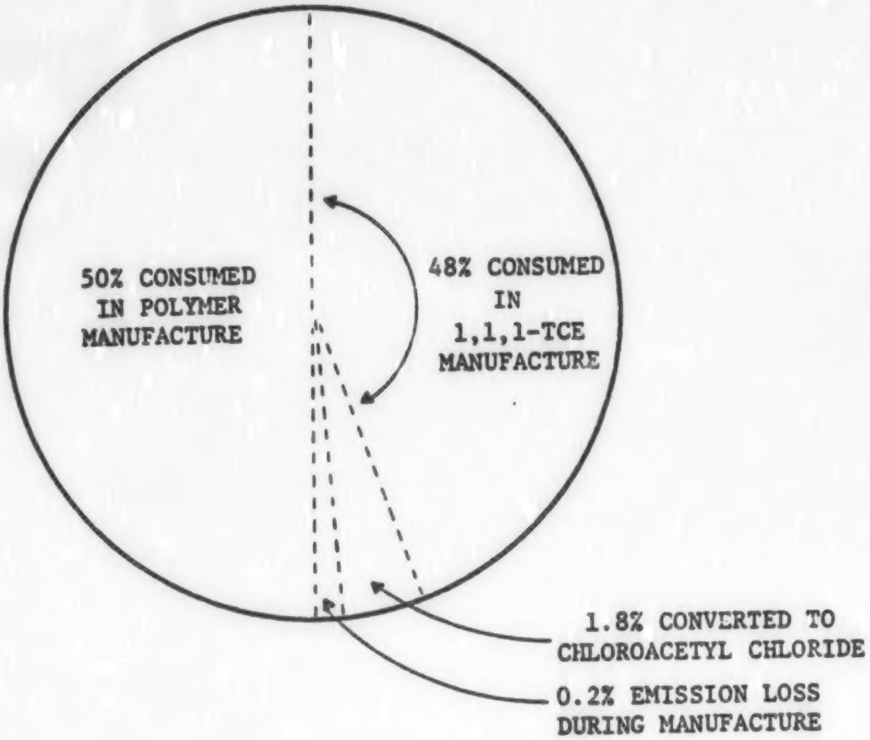


FIGURE 6-2. PERCENTAGE DISTRIBUTION OF VDC OUTPUT

manufacture, and no contamination of the purified product that is used as an intermediate for further chemical reactions.

6.2.3 VDC Consumption in Polymerization

Many types of copolymers are produced in the United States. Approximately 70 percent of all VDC-containing polymers manufactured are produced by one company. The balance are manufactured by about 12 companies.

The copolymers fall into the following groups:

(1) Resins for manufacture of saran films

(2) Resins for molding and extrusion

(3) Resins for solvent coating of cellophane and similar products

(4) Latexes for barrier coating of paper, paper products, glassine and plastic film

(5) Latexes for carpet backing

(6) Modacrylic fiber production

(7) Exported products

In the polymerization process that reacts VDC monomer, substantially all the VDC monomer is converted to polymers. There are environmental losses to the air, water and landfills as well as some contamination of the polymer products.

The majority of losses to the atmosphere occur during the polymerization process. These were calculated to be about 560,000 pounds in 1976.

The liquid and solid waste losses of VDC monomer result from the sewering of bad polymer batches or cleaning of polymer reactors and storage vessels. In these instances, the monomer VDC is present as a contaminant of the polymer.

Industry sources indicate that the domestic total of these losses of VDC amount to perhaps 3,600 to 4,000 pounds per year.

VDC input to polymerization processes has been estimated to be 135 million pounds in 1976, divided into the following end use categories:

	VDC INPUT MILLIONS OF LBS.
Resins for Saran Film	37.7
Resins for Molding & Extrusion	4.8
Resins for Solvent Coating	19.2
Latexes for Barrier Coatings	33.2
Latexes for Carpet Backing & Miscellaneous Applications	8.6
Modacrylic Fiber	10.0
Export	21.8
TOTAL	135.3

The data presented represents the input of VDC monomer to polymerization processes. Process losses to the environment and waste polymers have been prorated among the various end use categories.

VDC output from polymerization processes in each end use category would be somewhat smaller as discussed in Section 6.3.

6.2.4 VDC Output From Polymerization Process

The VDC output from polymerization processes comprise essentially direct atmospheric losses plus VDC contamination of polymeric materials that are sold, sewered or disposed into land fills. The direct atmospheric losses have been estimated to be 560,000 pounds per year.

PVDC polymerization products are contaminated with between 10 and 75 ppm VDC monomer depending on the type of polymer.

Resins for manufacture of films; solvent coating; molding and extrusion processes are reported by the manufacturers to contain a maximum of 20 ppm monomer as sold. This would amount to about 1,100 pounds per year, based on resin sales of 57.5 million pounds in 1976.

Latexes for barrier coatings using present technology contain about 50 ppm of monomer. Based on 1976 estimated sales of barrier coatings containing 30.88 million pounds of PVDC, these barrier latexes are estimated to contain 1,544 pounds VDC monomer.

Specialty latexes are reported to contain 13 pounds of VDCM per million pounds of PVDC. Based on an 8 million pound PVDC content of these latexes, the residual monomer would not exceed about 100 pounds annually.

It is estimated that about 7.8 million pounds of PVDC are sewered as a waste of polymerization processes. These wastes contain an estimated 3,600 to 4,000 pounds of VDC monomer.

The total VDC output from polymerization operations is thus that lost to the environment as a result of polymerization processes, and that contained as a contaminant in the finished polymer latexes or resins.

Approximately 566,500 lbs of VDC, out of a total input of 135 million pounds, remain unconverted from polymerization processes. This is equivalent to 99.6% utilization of VDC monomer in the polymerization operations.

6.2.5 VDC Input/Output in Converting Processes

Converting processes include coating of paper, glassine and paper products; coating of cellophane and plastic films; extrusion of films and monofilament fibers, and molding operations.

VDC input to this sector consists of the residual VDC monomer content of the latex or resin used in these operations. In the previous section this was calculated to be about 2,700 pounds.

Industry sources indicate that about 95% (or 2,500 lbs.) was lost to the atmosphere during converting operations.

On this basis, some 200 pounds of VDC monomer remains in the approximately 125 million pounds (PVDC content) of film or coated products produced by the many converting companies in the United States. This is equivalent to 1.6 ppm VDCM in the PVDC content of the copolymers consumned.

6.3 POLYVINYLIDENE CHLORIDE INPUT/OUTPUT SUMMARY

In section 6.2.3, it was shown that about 135 million pounds of VDC monomer were fed into polymer production facilities. Approximately 125 million pounds of PVDC-containing polymer were sold for the uses indicated. The balance was lost in the form of monomer vented to the air or in copolymers sent to sewerage ponds or land fills. Industry sources reported that of the 135 million pounds of VDC input, about 560,000 pounds were lost directly to the atmosphere and 7.8 million pounds* lost as solid or latex emulsion going to sewerage ponds or land fills.

Table 4-1 on page 92 summarizes the end uses of the 125 million pounds that are consumed in various converting and food packaging operations, as a flame retardant carpet backing and as a modacrylic fiber.

In addition to the PVDC manufactured in the U.S., it is reported that about 3 million pounds of resin are imported annually from Japan bringing total U.S. consumption to about 128 million pounds in 1976.

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*VDC lost as monomer or in polymerized form.

Converting processes usually refer to those processes in which a flexible material is "converted" into the finished package. These operations are notoriously wasteful of material. Between 25 and 50% of the input packaging materials are normally lost and disposed in land fills or incinerators.

Taking an average of 25% converting loss on all PVDC or PVDC-containing materials manufactured and consumed in the U.S., then about 26 million pounds out of 105 million* are wasted at the converting level and only about 79 million pounds of PVDC containing materials enter the end-use sectors where there is consumer contact. These 79 million pounds of PVDC materials are estimated to contain less than 200 pounds of VDC monomer (2.5 ppm).

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*Excludes 20 million pounds exported

SECTION VII. SUMMARY OF CHEMICAL LOSSES

This section will discuss briefly losses of VDC monomer to the atmosphere, to water streams or to solid waste disposal operations. PVDC losses will not be considered in this section except for those cases where it is a carrier of residual VDC monomer. The losses are summarized in Table 7-1.

7.1 AIR EMISSIONS

VDC emissions to the atmosphere occur from the following sources:

(1) Manufacture of VDC
(2) As a residual in 1,1,1-TCE manufactured from VDC
(3) Polymerization operations
(4) Polymer conversion operations
(5) Migration of residual VDC from polymer products

These losses have been estimated and shown in Table 7-1 and for 1975, they have been calculated to be 1,132,920 lbs.

TABLE 7-1. SUMMARY OF ENVIRONMENTAL LOSSES, 1975

	VDC, lbs./yr.		
	Air	Water	Solid
Monomer Production	550,000	0	0
1,1,1-TCE Production	17,500	0	0
Chemical Intermediate Production	0	0	0
Polymerization - Total	560,000	4,100	0
Converting Plants	2,500	0	180
Barrier Coating	2,000	0	0
Cellophane Coating	320	0	0
Film Extrusion	200	0	0
Rug Backing	200	10	0
Modacrylic	200	0	0
TOTAL	1,132,920	4,100	180

It is believed that the quantity in 1976 has remained at about this level, or decreased slightly. By 1978, this quantity should be reduced by about 150,000 pounds when PPG starts operation of a new 1,1,1-TCE plant that does not use VDC as the raw material. According to industry reports, some continued technology improvements can be expected in reducing emissions in both manufacturing and polymerization operations. However, these reductions are not expected to be more than 10 to 20% without the expenditure of substantial quantities of capital.

It is believed that technological developments leading to further reduction of residual VDC monomer in polymer products to substantially below the current 50 ppm in latexes and 10 ppm in resins can only be achieved by very substantial capital investments. 98% of the VDC monomer contained in latexes or resins is released during converting operations. Based on current technology, this amounts to about 2,000 pounds annually.

The total monomer residual in finished products as they reach the consumer is estimated to be on the order of 300 to 400 lbs. per year, or less than 3 ppm. In some instances, as with saran films or saran coated cellophane, these levels have been reported to be less than 1 ppm.

This quantity of monomer would be released very slowly. The rate of release is a function of the rate of migration through the polymer. It is believed that the rate is so slow, that the bulk of the residual VDCM in the converted product remains with the product and is disposed along with the polymer to solid waste disposal systems.

7.2 SOLID WASTE DISPOSAL

The amount of VDC monomer lost in solid form is limited to the small residual quantities of monomer remaining in the polymeric products that are manufactured and sold as "converted" materials. These include:

(1) Saran film and film laminates
(2) Saran coated paper and paper products
(3) Saran coated plastic film products
(4) VDC copolymers used as carpet backing
(5) Molded and extruded saran products other than film
(6) Modacrylic fibers

Based on information supplied by industry sources, residual VDC monomer in these converted products as manufactured ranges from below 1 ppm to 3 ppm. If for purposes of this study, an average value of 1.5 ppm is used, and the entire quantity of VDC polymerized is assumed to be disposed in municipal solid waste disposal operations, then the maximum potential quantity of VDC monomer contained in solid wastes would be of the order on 1.5 ppm x 120 million pounds or 180 pounds per year for 1975/1976.

Some industry estimates have been reported as high as 220 pounds.

Industry sources indicate there is no evidence to show that monomer VDC accumulates in the environment. Rather, on exposure to oxygen, it tends to form peroxides which decompose spontaneously (Gay, et al., 1976).

7.3 LIQUID EFFLUENT EMISSIONS

Liquid effluent containing VDC monomer is limited to that occurring as a result of polymerization operations. This consists of:

(1) VDC monomer contained in waste polymer sludges arising from reactor cleaning and bad batches.

(2) VDC monomer dissolved in condensed water streams obtained by condensation of gases obtained during stripping operations.

The amount of this has been reported to be between 375 and 430 ppm of PVDC wasted. The amount of PVDC sent to latex ponds, sludge sewers or plant liquid waste disposal systems has been estimated to be in 1975, about 7.0 million pounds and in 1976, about 7.4 million pounds.

Based on these data, it is estimated that between 2,600 and 3,000 pounds per year of VDC monomer are lost in liquid waste streams.

Substantially all of this loss is either bio-degraded in the chemical waste disposal units or diffuses into the atmosphere where it is oxidized.

7.4 POTENTIAL FOR INADVERTENT PRODUCTION IN INDUSTRIAL PROCESSES

VDC monomer, as has been discussed in Section III, can be produced as a co-product (by-product) during the chlorination, hydrochlorination or dehydrochlorination of ethane, ethylene or acetylene, or any of their chlorinated derivatives. Except for those processes in which VDC is removed from the product stream and recovered for its economic value, current manufacturing procedures recycle the intermediate chlorinated ethanes, ethylenes or acetylenes (such as VDC) for further reaction into the desired chlorinated chemical.

The potential for this to occur as part of an overall reaction process is not insignificant. However, the potential for this product to remain as a contaminant of the final chlorinated chemical that is recovered for further use or for sale is believed to be very unlikely. Should it occur, as in the case of 1,1,1-TCE manufactured from VDC, it would not be present beyond an order of magnitude of a few ppm as a maximum.

There does not seem to be any likelihood for producing VDC in the environment. It is synthesized under conditions of temperature, pressure and catalyst from ethylene dichloride in a complex series of reaction steps which can include the formation of vinyl chloride. The alternate method is the dehydrochlorination of 1,1,2-trichloroethane in the presence of an alkali. None of these chemicals occur naturally in the environment in contact with chlorine or hydrogen chloride under conditions that would cause them to react to form VDC.

7.5 SUMMARY OF GENERAL ENVIRONMENTAL POLLUTION BY VDC

VDC emissions and losses in 1975 from all sources amount to approximately 1,132,920 lbs; of this, an estimated 99+% enters atmosphere.

It is estimated that perhaps 3,000 pounds annually could enter the environment as a liquid effluent and a probable maximum of 200 to 300 pounds per year are disposed as a component of solid waste materials.

Approximately 550,000 lbs. of VDC are vented to the air by three manufacturing sites. An additional 568,000 lbs. of VDC enter the atmosphere from 13 polymerization sites.

The bulk of liquid effluent VDC monomer contamination occurs at the 13 polymerization sites.

Negligible environmental pollution of the environment occurs from conversion operations or from ultimate disposal of the final packaging materials products.

7.6 SUMMARY OF OTHER CHEMICALS RELEASED TO THE ENVIRONMENT

By-products or co-product chemicals that could be released to the environment during the manufacture of VDC can include other chlorinated hydrocarbons such as ethylene dichloride, hydrogen chloride.

In processes that use VDC as a raw material to produce other chlorinated hydrocarbons such as 1,1,1-TCE, and chloroacetylchloride, it is conceivable that these chemicals could also be released to the environment.

The comonomers of VDC could be released jointly with VDC from polymerization and conversion processes.

The bulk of VDC copolymers contain 70 to 95% VDC, the balance comprised of such monomers as vinyl acetate, acrylonitrile, acrylic and methacrylic acids. These comonomers can also be emitted together with VDC during polymerization processing. However, because they are present in the monomer mixture in lesser quantities, it is unlikely that they would be present in significant quantities in polymerization wastes (air, liquid or solid).

SECTION VII. REFERENCES

Gay, B.W., P.L. Hanst, J.J. Bufalini, and R.C. Noonan (1976), "Atmospheric Oxidation of Chlorinated Ethylenes," Environ. Sci. Tech., 10(1), 58-67.